Published in Journals: Coatings, Materials, Nanomaterials, Colloids and Interfaces

Topic Reprint

Advances in Functional Thin Films

Edited by Ricardo López Antón, José María De Teresa and Sion Federico Olive Méndez

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Topic Editors

Ricardo Lopez Anton Jose Maria De Teresa Sion Federico Olive Méndez



Topic Editors Ricardo Lopez Anton Department of Applied Physics University of Castilla-La Mancha Ciudad Real Spain

Jose Maria De Teresa Instituto de Nanociencia y Materiales de Aragón CSIC-Universidad de Zaragoza Zaragoza Spain Sion Federico Olive Méndez Centro de Investigación en Materiales Avanzados, SC Chihuahua Mexico

Editorial Office MDPI AG Grosspeteranlage 5 4052 Basel, Switzerland

This is a reprint of the Topic, published open access by the journals *Coatings* (ISSN 2079-6412), *Materials* (ISSN 1996-1944), *Nanomaterials* (ISSN 2079-4991) and *Colloids Interfaces* (ISSN 2504-5377), freely accessible at: https://www.mdpi.com/topics/Z4V17Y7WDS.

For citation purposes, cite each article independently as indicated on the article page online and as indicated below:

Lastname, A.A.; Lastname, B.B. Article Title. Journal Name Year, Volume Number, Page Range.

ISBN 978-3-7258-3033-6 (Hbk) ISBN 978-3-7258-3034-3 (PDF) https://doi.org/10.3390/books978-3-7258-3034-3

Cover image courtesy of Jose Maria De Teresa

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About the Editors

Ricardo Lopez Anton

Ricardo Lopez Anton is an associate professor at the University of Castilla-La Mancha (UCLM) and a member of the group of Magnetic Materials at the Instituto Regional de Investigación Científica Aplicada (IRICA-UCLM). He is currently part of the board of the Club Español de Magnetismo (CEMAG, a national association of researchers of magnetic materials). He has worked previously at SIEMENS AG (Germany), University of the Basque Country (UPV/EHU, Spain), and the ISIS Neutron and Muon Source (Rutherford Appleton Laboratory, UK). His main research interests are nanomaterials, magnetic materials, thin films, and multilayers. He has published more than 60 research articles on those topics.

Jose Maria De Teresa

Jose Maria De Teresa leads the group of Nanofabrication and Advanced Microscopies (NANOMIDAS) at the Instituto de Nanociencia y Materiales de Aragón (INMA, CSIC-Universidad of Zaragoza) in Spain. He is the coordinator of the Spanish network on Nanolithography (NANOLITO) and of the FIB-SEM area in the Spanish National facility for Advanced Microscopies. He is the Chair of the Condensed Matter Division Board in the European Physical Society. His main research interests are nanofabrication with focused electron and ion beams, magnetic nanostructures, nano-superconductivity, and quantum technologies. He has published 240 research articles on those topics and delivered more than 100 invited conferences. He is a Fellow of the American Physical Society (2021), a Fellow of the European Physical Society (2023), and a Fellow member of the European Academy of Sciences (EURASC).

Sion Federico Olive Méndez

Sion Federico Olive Méndez is a professor of the Research Centre of Advanced Materials and Head of the Materials Physics Department (2017) in Chihuahua, Mexico. He is member of the Mexican National Researchers System level 3. His main research interests are the growth of single crystal thin films by magnetron sputtering, magnetic anisotropy, anomalous and Topological Hall effects and non-collinear antiferromagnets. He has published more than 50 research articles.





Article **Plasma-Assisted Atomic Layer Deposition of IrO**₂ **for Neuroelectronics**

Valerio Di Palma^{1,*}, Andrea Pianalto¹, Michele Perego², Graziella Tallarida², Davide Codegoni³ and Marco Fanciulli^{1,*}

- ¹ Department of Materials Science, University of Milano Bicocca, Via R. Cozzi 55, 20125 Milano, Italy
- ² CNR-IMM Unit of Agrate Brianza, Via C. Olivetti 2, 20864 Agrate Brianza, Italy
 - ³ STMicroelectronics, Via C. Olivetti 2, 20864 Agrate Brianza, Italy
 - * Correspondence: valerio.dipalma@unimib.it (V.D.P.); marco.fanciulli@unimib.it (M.F.)

Abstract: In vitro and in vivo stimulation and recording of neuron action potential is currently achieved with microelectrode arrays, either in planar or 3D geometries, adopting different materials and strategies. IrO₂ is a conductive oxide known for its excellent biocompatibility, good adhesion on different substrates, and charge injection capabilities higher than noble metals. Atomic layer deposition (ALD) allows excellent conformal growth, which can be exploited on 3D nanoelectrode arrays. In this work, we disclose the growth of nanocrystalline rutile IrO₂ at T = 150 °C adopting a new plasma-assisted ALD (PA-ALD) process. The morphological, structural, physical, chemical, and electrochemical properties of the IrO₂ thin films are reported. To the best of our knowledge, the electrochemical characterization of the electrode/electrolyte interface in terms of charge injection capacity, charge storage capacity, and double-layer capacitance for IrO₂ grown by PA-ALD was not reported yet. IrO₂ grown on PtSi reveals a double-layer capacitance (*C*_{dl}) above 300 μ F·cm⁻², and a charge injection capacity of 0.22 ± 0.01 mC·cm⁻² for an electrode of 1.0 cm², confirming IrO₂ grown by PA-ALD as an excellent material for neuroelectronic applications.

Keywords: pseudocapacitive; atomic layer deposition; IrO₂; neuroelectronics

1. Introduction

The investigation of neural networks in vitro is fundamental for the understanding of the mechanisms involved in neurological diseases such as Alzheimer's. In this context, the study of the short- and long-distance interactions between neurons is possible thanks to the development of microelectrode arrays (MEAs), which can be used for the stimulation of neurons and the recording of neuronal signals [1]. MEAs are realized, usually on rigid substrates, either in planar or 3D geometries. The latter approach has been shown to provide a better physical and electrical coupling between the neurons and the electrodes.

The electrical interaction between MEAs and neurons can take place according to two main different charge transfer mechanisms that are determined by the electrical properties of the electrode's material. The so-called capacitive charge transfer takes place when a dielectric material, which forms a capacitor at the electrode/electrolyte interface, is polarized, and it transfers the polarization to the electrolyte. The other mechanism, commonly occurring for metallic electroles, consists of a direct, Faradaic transfer of charges between the electrode and the electrolyte [2]. Among the Faradaic charge transfer mechanisms, it is possible to distinguish between the irreversible transfer, generally unwanted, and the reversible transfer. The latter mechanism is generally referred to as pseudocapacitive, since it involves mass exchange at the interface electrode/electrolyte while the stability of the electrode is preserved, as for the capacitive charge transfer [2].

IrO₂ has been widely applied in the neuroelectronic field because of its pseudocapacitive behavior, along with good stability and non-toxicity [3–5]. Nevertheless, the electrical, physical, and chemical properties of the material depend also on the deposition method.

Citation: Di Palma, V.; Pianalto, A.; Perego, M.; Tallarida, G.; Codegoni, D.; Fanciulli, M. Plasma-Assisted Atomic Layer Deposition of IrO₂ for Neuroelectronics. *Nanomaterials* **2023**, 13, 976. https://doi.org/10.3390/ nano13060976

Academic Editors: Ricardo Lopez Anton, Jose Maria De Teresa and Sion Federico Olive Méndez

Received: 18 February 2023 Revised: 3 March 2023 Accepted: 6 March 2023 Published: 8 March 2023



Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). Electrodeposition of IrO_2 can cause the incorporation of the solvent, generally water, in the film so prepared. The consequence is the formation of a hydrated IrO_2 layer at the top of the electrode, which is less dense and thus prone to corrosion under working conditions [2]. For the same reason, the use of the so-called activated IrO_2 (AIROF) poses issues for the long-term stability of the electrode [6,7].

On the other hand, IrO_2 layers prepared by reactive sputtering for neuroelectronics are often quite thick (about 100 nm or more), posing issues with the amounts of such a rare metal required for electrode fabrication [3,8,9]. In addition, physical deposition methods do not provide conformal growth on 3D substrates with significant aspect ratios. An alternative approach for the deposition of IrO_2 onto MEAs can be offered by atomic layer deposition (ALD), a thin film deposition method applied in several fields such as micro- and nanoelectronics, spintronics, photovoltaics, electrocatalysis, and neuroelectronics. A key feature of ALD is the self-limiting behavior of the reactions involved, which enables good control of the thickness, high reproducibility, good quality in terms of impurity incorporation, and excellent conformality, i.e., uniformity even onto 3D complex structures [10,11]. ALD also offers the possibility of developing low-temperature processes compatible with flexible substrates such as polydimethyl-siloxane (PDMS).

Only a few reports on the application of IrO₂ grown by ALD for neuroelectronics have been published so far [5,12]. In addition, the electrochemical characterization of the electrode/electrolyte interface in terms of charge injection capacity, charge storage capacity, and double-layer capacitance for IrO_2 grown by ALD is still missing. Regarding ALD processes reported in the literature, IrO2 is mainly deposited via thermal ALD, using O2 or O_3 as a reactant [13–17], while the use of plasma is still very limited. The use of plasma as a co-reactant can be beneficial in several aspects, besides the advantages already mentioned for ALD. The plasma is generally obtained in the gas phase by an electric field, which accelerates the electrons. These hot electrons then collide with neutral species, generating ions, radicals, and UV photons [18]. The high reactivity of plasma can be beneficial in removing impurities, enabling depositing materials with better electronic properties [18–21]. Furthermore, the high energy provided to the substrate by the plasma allows it to achieve deposition with a lower thermal budget [18,22-24]. Therefore, the use of a plasma-assisted process, instead of thermal ALD, can be beneficial for the integration of the process in the device fabrication, since plasma enables the deposition at lower temperatures (<200 °C). This aspect can be relevant for the fabrication of multi-channel MEAs for neuroelectronics.

There are few reports, to the best of our knowledge, using a plasma-assisted ALD (PA-ALD) process for the preparation of IrO₂. In 2007 Choi et al. [25] reported PA-ALD of IrO₂ nanodots using ethylcyclopentadienyl cyclo-hexadiene iridium [(EtCp)Ir(CHD)] dissolved in ethyl cyclo-hexane as a precursor, and a mix of O₂ and H₂ plasma as co-reactant. The same combination of precursor and co-reactant was applied in 2014 by Kim et al. [26] for PA-ALD of IrO₂ nanodots. It is worth mentioning that (EtCp)Ir(CHD) was originally designed and synthesized by Kawano et al. [27] in 2004 as a precursor for the metal–organic chemical vapor deposition (MOCVD) of Ir. Recently, Simon et al. [12] have reported a new PA-ALD of IrO₂ (on silicon with its native oxide) using O₂ plasma as a reactant and (Methylcyclopentadienyl) (1,5-cyclooctadiene) Iridium(I) [(MeCp)Ir(CDD)].

In this work, we report on a novel PA-ALD approach for the growth of IrO_2 . The process is based on the application of a mix of Ar/O_2 plasma as a reactant in combination with (EtCp)Ir(CHD) as a precursor. Compared to previous works on PA-ALD of IrO_2 using (EtCp)Ir(CHD), we did not have to dissolve the precursor in cyclo-hexadiene or feed the plasma source with H_2 gas. The ALD process is characterized in situ by spectroscopic ellipsometry (SE). In situ SE is a key tool for the characterization of ALD processes, since it is able to monitor thickness changes in the films deposited down to the atomic scale [28–31]. The determination of the thickness via SE requires modeling the dielectric function of the film. For the specific case of rutile IrO_2 , a Drude–Lorentz oscillator was selected, generally applied for modeling the absorption of light of conductive materials [28–31].

The chemical, physical, and electrochemical properties of the IrO_2 thin films have been fully characterized to assess key functionalities relevant to neuroelectronics. Specifically, an extensive electrochemical characterization has been performed, providing key parameters for neuroelectronics, such as the double-layer capacitance, the charge storage capacity, and the charge injection limit. Furthermore, the interpretation of the impedance spectroscopy measurements has been corroborated by the cyclic voltammetry measurements. This last aspect is not very common in the literature on neuroelectronics and can be of broader interest in the electrochemical field.

PtSi has been selected as a conductive substrate for the deposition of IrO₂. The choice of the substrate is motivated by the planned integration of IrO₂ onto vertical nanopillar arrays to be used as scalable nanoelectrodes fabricated starting from silicon nanopillars [32].

2. Materials and Methods

IrO₂ deposition was performed using a PICOSUN R-200 Advanced ALD system, equipped with a remote inductively coupled plasma source. The base pressure of the ALD reaction chamber is within the range of 0.2–4.0 hPa. The plasma source operates in the range of 1.9–3.2 MHz, with the plasma power adjustable from minimum of 300 W to maximum of 3000 W. The distance between the plasma source and the sample holder is about 75 cm, in order to reduce any possible damage to the substrate from highly energetic ions. (EtCp)Ir(CHD) (99%), from Strem Chemicals, was kept in a stainless steel cylinder heated to 100 °C, while the line from the cylinder to the deposition chamber was heated to 120 °C. (EtCp)Ir(CHD) precursor should be handled with care, since it causes skin and eye irritation and may cause respiratory irritation. N₂ gas (99.9999%), used as carrier for the precursor, was flowed at 200 sccm. A mix of Ar gas (99.9999%) and O₂ gas (99.9999%), flowing at 40 sccm and 190 sccm, respectively, was used to feed the plasma. During the plasma step, the power of the plasma source was set to 2500 W.

The ALD recipe starts with the dosing of (EtCp)Ir(CHD) for 6 s, followed by 15 s of purge. Then, the mixture of Ar/O_2 is flowed through the plasma source for 1 s in order to stabilize the flow before igniting the plasma for 40 s. Afterward, a purge step of 4 s closes the ALD cycle.

Film Sense FS-1TM ellipsometer system was used for in situ and ex situ characterization of thickness and optical constants of the deposited IrO_2 layer. The fitting of thickness and optical constants of IrO_2 thin films was performed using a Drude–Lorentz oscillator.

ALD-prepared IrO_2 thin films were characterized by X-ray diffraction in grazing incidence mode (GI-XRD), transmission electron microscopy (TEM) and energy dispersive spectroscopy (EDS), time-of-flight secondary ion mass spectrometry (TOF-SIMS), X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM).

Transmission electron microscopy (TEM) techniques were conducted on electrontransparent lamellae obtained by focused ion beam (FIB). The alloy microstructure was observed by bright-field TEM and high-angle annular dark-field STEM (HAADF-STEM), while high spatial resolution chemical analyses were carried out by energy dispersive spectroscopy (EDS). The lamellae were obtained using a Thermofischer Helios G5UX FIB. Low energy milling was used during the final thinning steps to limit heating and ballistic effects of ion irradiation on alloy film. The TEM images were performed with a Thermofischer Themis Z G3 aberration-corrected transmission electron microscope equipped with an FEG electron gun operating at 200 kV acceleration voltage. To minimize the electron beam damage, all the TEM/STEM images and EDS maps were acquired with a low beam current (0.5 nA). The EDS measures were carried out using a Dual-X sensor made of two detectors of 100 mm². The elemental maps were acquired and elaborated by Velox software.

GI-XRD was performed on a Rigaku Smartlab SE equipped with a Cu Ka source (Ka1 = 1.540598) operating at 40 KV and 30 mA. Data were collected under parallel beam conditions, at the angle of incidence of 0.2° , in the range of 20° – 50° .

ToF-SIMS profiles were performed using a dual beam IONTOF IV system operating in negative polarity. Sputtering was accomplished using Cs^+ ions at 1 keV (113 nA) and

rastering over a 300 \times 300 mm² area. Analysis was performed by means of Ga⁺ ions at 25 keV (1.2 pA) rastering over a 50 \times 50 mm² area.

XPS analysis was performed on a PHI5000 Versaprobe III system equipped with a monochromatic Al Ka X-ray source (1486.6 eV) and a concentric hemispherical analyzer with a take-off angle of 45° . Survey spectrum was acquired with a band-pass energy of 280 eV. High-resolution spectra were acquired with a band-pass energy of 55 eV. C 1*s* signal at 284.5 eV was used to correct the binding energy scale.

Film surface morphology was analyzed by atomic force microscopy, using a commercial system (Bruker Dimension Edge). Measurements were carried out in non-contact mode using sharp silicon probes with typical tip radius of 10 nm and resonance frequency of approximately ~320 kHz. Several square scans (1- to 5-micron side) were taken at various surface locations. The acquired data were analyzed by Gwyddion (http://gwyddion.net/; accessed on 7 March 2023) to derive the root mean square (RMS) roughness and the correlation length (L). RMS accounts for the height fluctuations of the surface features, whereas the correlation length is the measure of the length beyond which surface heights are not significantly correlated and it was estimated by the gaussian fitting of the height–height correlation function (see Equations (S1)–(S3), Figures S1 and S2 in the supporting information). The surface parameters reported are the average values over the available data, and the dispersion of these values is reported as the experimental error.

Electrochemical tests were performed using a double-sided-magnetic mount photoelectrochemical cell from Redoxme. Unless differently specified, the electrode area is 1.0 cm². Electrochemical impedance spectroscopy (EIS) was performed using a Zurich Instruments MFIA impedance analyzer, applying a test signal of 100 mV in the frequency range from 0.1 Hz to 100 kHz. EIS characterization of the interface IrO_2 /electrolyte was performed in a two-electrode configuration, with two IrO_2 samples facing each other in electrical contact through the electrolyte. The phosphate buffer (PBS) used as electrolyte for all the electrochemical characterizations was prepared by diluting 10 mL of PBS $10 \times$ purchased from Sigma-Aldrich with 90 mL of deionized water.

Cyclic voltammetry (CV) and voltage transient measurements (VT) were performed using a BioLogic VMP3 multi-channel potentiostat in a three electrodes configuration, i.e., the sample under study as working electrode (WE), an Ag | AgCl wire as reference electrode (RE) and a Pt wire as counter electrode (CE). The Ag | AgCl was selected as reference electrode since it is commonly applied in the field of neuroelectronics [3]; thus, it makes it more straightforward to compare electrochemical characterization performed in this work with the literature.

3. Results and Discussion

3.1. Plasma-ALD of IrO₂

The in situ characterization of ALD of IrO₂ (on PtSi) via spectroscopic ellipsometry is shown in Figure 1. From Figure 1a, it is possible to see that, after a nucleation delay of about 50 cycles, the process exhibits linear growth. From the fitting of the experimental data, the growth-per-cycle (GPC) of the process is 0.28 ± 0.01 Å at 150 °C. The value obtained is lower than the value of 0.66 Å reported recently by Simon et al. [12] for PA-ALD of IrO₂. Nonetheless, the different GPC could be explained by the use of different precursors, i.e., (EtCp)Ir(CHD) in this work and (MeCp)Ir(COD) in the work of Simon et al. [12]. On the other hand, the reports of Choi et al. [25] and Kim et al. [26] on PA-ALD of IrO₂ focus on the deposition of nanodots; therefore, the GPC value of the process is not specified. From Figure 1b, it is possible to appreciate the thickness changes taking place during each ALD dosing step. The thickness shows a steep increase during the dosing of the (EtCp)Ir(CHD) precursor, due to the adsorption of the precursor on the substrate. Subsequently, during the plasma dosing, the thickness decreases because of the removal of the precursor's ligands.



Figure 1. (a) Time-resolved in situ spectroscopic ellipsometry measurements during 600 ALD cycles of IrO₂, at 150 °C onto PtSi. The process exhibits linear growth after a nucleation period of about 50 cycles, corresponding to about 55 min on the time scale. (b) Enlargement of the in situ measurement reported in (a), showing the characteristic step-like behavior found for the ALD process, with a thickness increase due to the precursor dosing and a subsequent thickness decrease during the plasma dosing due to the removal of ligands.

The saturation of each ALD dosing step was tested by independently changing the dosing times of precursor and co-reactant. Figure 2 shows the GPC as a function of the dosing time for the (EtCp)Ir(CHD) (Figure 2a) and for the plasma (Figure 2b), respectively. The ALD process shows saturation for 6 s of precursor dosing and 40 s of plasma dosing.



Figure 2. Saturation curves for ALD of IrO₂. (a) GPC as function of the (EtCp)Ir(CHD) dosing time. (b) GPC as function of the O₂ plasma dosing time. Dashed lines are a guide to the eyes.

3.2. Physical and Chemical Characterization of IrO2

The crystallinity of the ALD-prepared IrO₂ thin films was investigated by grazing incidence X-ray diffraction (GI-XRD). Figure 3 shows that IrO₂ prepared by ALD at 150 °C reveals the characteristic pattern of IrO₂ in the rutile phase, with the three peaks corresponding to the <110>, <101>, and the <200> planes, as reported in the literature [33]. The full-width half maximum and the θ of the three peaks were used to determine, by means of Scherrer's formula, the average grain size of IrO₂ in the thin film [34,35]. Assuming the shape factor K = 0.9 and knowing the wavelength of the Cu Ka source λ = 1.540598 Å, the average grain size of ALD-prepared IrO₂ thin film was determined to be 5.3 nm ± 0.4 nm.



Figure 3. GI-XRD results for IrO₂ thin film prepared by 600 ALD cycles, corresponding to about 14.8 nm (red line). Angle of incidence ω is 0.2°. The results are compared with the XRD pattern for rutile IrO₂ powder (black line) calculated with the Mercury Software using the structure deposited on the Cambridge Structural Database as ICSD 640885, deposition number 1759474 [36,37]. The average grain size of IrO₂, determined by Scherrer's formula, is 5.3 nm \pm 0.4 nm.

Figure 4 shows the TEM cross-section and TEM-EDS of IrO₂ grown on PtSi/Poly-Si/SiO₂/Si. Figure 4a shows a TEM image of the IrO₂ layer, clearly visible because of the difference in Z-contrast with respect to the PtSi substrate. The layer is homogenous with a thickness of about 13 nm, in line with SE measurements. Figure 4b shows EDS color maps of Ir (yellow), O (green), Pt (purple), and Si (cyan) of the specimen. The Ir-L line, O-K line, Pt-L line, and Si-K line, respectively, were used for the construction of the color maps. The analysis reveals a continuous and conformal IrO₂ layer on PtSi. Considering the surface roughness of PtSi, the interface between IrO₂ and PtSi is sharp, with no clear indication of interdiffusion between the two layers. The surface roughness of the underlying substrate has a strong influence on the surface morphology of the IrO₂ deposited, as suggested by AFM measurements performed on IrO2 grown onto Al2O3 on c-Si (see Figure S3 in the supporting information). Specifically, the RMS of IrO_2 on Al_2O_3 was 0.7 nm \pm 0.3 nm, way lower compared to the RMS of IrO₂ grown onto PtSi (3.5 nm \pm 0.3 nm). The EDS line profile in Figure 4c clearly shows Ir and O peaks related to ALD thin film, while the increasing Pt signal on the surface of IrO_2 is due to the Pt deposited as a contrast layer during the specimen preparation. No further contamination from other elements was detected in the IrO₂ film within the sensitivity limit of the EDS technique.

ToF-SIMS depth profile of the ALD-prepared IrO₂ thin film, shown in Figure 5, confirms the presence of a thin, but homogeneous, IrO₂ layer on top of the PtSi substrate. ¹⁹³IrO⁻ secondary ion signal and ¹⁹⁵Pt⁻ and ³⁰Si⁻ secondary ion signals are reported as markers of the IrO₂ film and PtSi substrate, respectively. These signals clearly indicate no diffusion of Pt and Si from the substrate into the IrO₂ film during the ALD growth. The broadening of the ¹⁹³IrO⁻, ¹⁹⁵Pt⁻, and ³⁰Si⁻ secondary ion signals at the IrO₂/PtSi interface is fully consistent with the roughness of the PtSi surface that was highlighted by the TEM analysis shown above in Figure 4. No C contaminations were detected in the IrO₂ film, within the sensitivity limit of the technique, confirming the good quality in terms of impurities for the IrO₂ thin film prepared by ALD.



Figure 4. (a) TEM cross-section image of IrO_2 on PtSi. (b) EDS mapping of IrO_2 on PtSi. (c) Linescan composition map of IrO_2 on PtSi. The analysis reveals a continuous and conformal IrO_2 layer on PtSi. The Pt detected by EDS on the surface is due to the deposition of Pt as an electronic contrast layer during the specimen preparation.



Figure 5. ToF-SIMS depth profiles of the IrO₂ film deposited on PtSi. ¹⁹³IrO⁻ secondary ion signal indicates the presence of a homogeneous IrO₂ film with negligible carbon contamination. ¹⁹⁵Pt⁻ and ³⁰Si⁻ signals are reported as markers of the PtSi substrate.

The results of the chemical characterization performed by XPS are reported in Figure 6. Figure 6a shows the survey spectrum of the IrO_2 film deposited on top of the PtSi substrate. The different core lines in the spectrum correspond to signals from the Ir and O atoms in the IrO₂ film. No signals from the underlying PtSi substrate were detected, further supporting the idea of a homogeneous IrO₂ film, perfectly covering the PtSi substrate. Figure 6b,c show high-resolution spectra of the Ir 4*f* and O 1*s* core lines, respectively. Since rutile-type IrO₂ is a metallic conductor, an asymmetric line shape is expected for the Ir 4*f* core lines. The high-resolution Ir 4*f* spectrum was fitted using a doublet of asymmetric functions with spin–orbit splitting of 3 eV to capture the main 4*f* lines and a doublet of Gaussians at 1 eV higher binding energy to capture the primary shake-up satellites. A secondary satellite of the Ir 4*f*_{5/2} peak at ~3 eV above the main line was introduced to obtain a satisfactory fitting of the experimental data, in agreement with previous results reported in the literature [33]. The position of the Ir 4*f*_{7/2} core line is determined to be 61.7 ± 0.1 eV. The high-resolution O 1*s* spectrum was fitted using asymmetric functions. The position of the O 1*s* core line is found to be 529.9 \pm 0.1 eV. Two additional Gaussian functions were introduced to correctly fit the experimental data. These functions account for hydroxyl groups (BE ~ 531.3 eV) and adsorbed water (BE ~ 532.4 eV) on the IrO₂ surface [38]. The binding energies of the Ir 4*f* and O 1*s* core lines are perfectly consistent with data available in the literature for rutile IrO₂ [33,38].



Figure 6. (a) Survey spectrum of the IrO₂ film deposited on top of the PtSi substrate. (b) Highresolution Ir 4*f* spectrum (open circles) of IrO₂ fitted with a doublet of asymmetric main lines (red) and a corresponding doublet of Gaussian functions corresponding to primary shake-up satellites (green). An additional Gaussian function (yellow) is introduced to account for secondary shake-up satellites. Calculated Shirley background (blue) is reported as well. Red line corresponds to the envelope of the fitting functions. (c) High-resolution O 1*s* spectrum (open circles) of IrO₂ fitted with an asymmetric main line (red) and two Gaussian-like lines corresponding to hydroxyl groups (green) and adsorbed water (yellow). Calculated Shirley background (blue) is reported as well. Red line corresponds to the envelope of the fitting functions.

The surface morphology of IrO_2 films is strictly related to the surface morphology of the supporting substrate. In Figure 7, AFM measurements of the IrO_2 surface and of

the bare PtSi surface are shown. IrO₂ (Figure 7a) has a marked granular morphology with an RMS roughness of 3.5 ± 0.3 nm and correlation length of 53 ± 3 nm, very similar to that of the PtSi substrate (Figure 7b. RMS roughness: 3.6 ± 0.2 nm; correlation length: 47 ± 3 nm). Thus, in the explored experimental conditions, IrO₂ film grows conformal to the PtSi substrate, replicating the corresponding surface profile.



Figure 7. AFM measurement of (a) IrO₂ deposited on PtSi and (b) PtSi surface morphology. Both images have scan size of 2 μ m × 2 μ m and image resolution is 512 × 512 points per line. The thickness of IrO₂ is about 14.8 nm.

3.3. Electrochemical Characterization

Electrochemical impedance spectroscopy (EIS) was used to characterize the charge transfer properties of the interface between the ALD-prepared IrO_2 and the electrolyte. Figure 8 shows the Bode plot, i.e., the module (Figure 8a) and the phase shift (Figure 8b) of the impedance measured as a function of frequency. The equivalent circuit used to fit the data was assembled with a constant phase element (CPE) to model the electrode/electrolyte interface, in series with a resistor (R_{sol}) used to model the bulk resistivity of the solution. The data analysis was performed using EIS Spectrum Analyser software [39]. The model applied fits the experimental data well, indicating that the charge transfer resistivity, generally used in parallel to the CPE for the modeling of the double layer, tends to infinity. This finding indicates that the ALD-prepared IrO₂ behaves in solution as an ideally polarized blocking electrode, i.e., no DC is flowing at the electrode/electrolyte interface. The parameters of the CPE, as reported in Table S1 (supporting information), can be used to estimate the double-layer capacitance (C_{dl}^{EIS}), according to the surface distribution model, using Equation (1) [40,41]:

$$C_{dl}^{EIS} = Q^{\frac{1}{n}} \cdot R_{sol}^{\frac{1-n}{n}} \tag{1}$$

where *Q* and *n* are the parameters defining the impedance of the CPE (see Equation (S4) in supporting information). For the results shown in Figure 8, the double-layer capacitance was calculated to be $301 \pm 4 \,\mu\text{F}\cdot\text{cm}^{-2}$. This value obtained for ALD-prepared IrO₂ is very promising, considering that the electrochemically active surface area influences the *C*_{dl}, and how in this work, IrO₂ was deposited onto a relatively flat substrate. As a comparison, a *C*_{dl} value of 270 μ F·cm⁻² has been reported for IrO₂ electrodeposited onto Ti felt [42].

In order to corroborate the C_{dl} value extracted from EIS data, the double-layer capacitance was determined via cyclic voltammetry (CV) as well. A series of CV measurements were carried out, varying the scan rate from 5 mV·s⁻¹ to 10 mV·s⁻¹ in the voltage range between 0.35 V and 0.45 V, where no faradaic processes are supposed to occur [9]. The results reported in Figure 9 show the capacitive cathodic current (I_c) and the capacitive anodic current (I_a) as a function of the voltage of the working electrode (E_{we}) for different scan rates. The double-layer capacitance can be calculated from the CV measurements via Equation (2) [9]:

$$C_{dl}^{CV} = i_{c/a} \cdot \left(\frac{dE}{dt}\right) \tag{2}$$

where $i_{C/a}$ is the capacitive current, cathodic or anodic, and dE/dt is the scan rate. As reported in Figure S4 (supporting information), the value of C_{dl}^{CV} obtained is about $341 \pm 1 \, \mu F \cdot cm^{-2}$ which is in good agreement with the value obtained by EIS, considering that two different methods, based on different working principles, were used. The high values of C_{dl} obtained for ALD-prepared IrO₂ can be explained by considering the good pseudocapacitive behavior of IrO₂ due to the oxidation/reduction of the Ir(III)/Ir(IV) species at the surface of the electrode [43,44]. It is worth mentioning that it is not common to find, in the literature on neuroelectronics, the comparison between EIS and CV for the characterization of the electrode/electrolyte interface and, more specifically, for the determination of the double-layer capacitance.



Figure 8. Electrochemical impedance spectroscopy data (black circle) and model (orange line) for the interface IrO_2 /electrolyte. (a) Module and (b) phase shift of the impedance as function of the frequency. The inset in (a) shows the equivalent circuit used for the modeling, i.e., a constant phase element (CPE) for the double layer, in series, with a resistor (R_{sol}) for the solution bulk.



Figure 9. Cyclic voltammograms of ALD prepared IrO_2 in the range 0.35 V-0.45 V for different scan rates. The values of capacitive cathodic current (I_c) and capacitive anodic current (I_a) at 0.40 V are used to determine the double-layer capacitance by the application of Equation (2). CV curves reported are acquired after 50 cycles of stabilization.

Cyclic voltammetry was then performed in order to determine the charge storage capacity (CSC) of ALD-prepared IrO_2 in the range of -0.6-0.8 V vs. Ag | AgCl. Figure 10 shows the cyclic voltammogram of IrO_2 thin film deposited onto PtSi (blue line) compared to the bare PtSi substrate (black line). The current density measured for the $IrO_2/PtSi$ electrode is much larger than the current density recorded for the PtSi substrate. Since the Faradaic contribution due to the oxidation and reduction of water is negligible below 0.8 V and above -0.6 V, the higher current density of IrO_2 over the PtSi substrate can be attributed to the pseudocapacitive behavior of IrO_2 , which allows accumulating a larger amount of charge.



Figure 10. Cyclic voltammograms of ALD-prepared IrO_2 deposited onto PtSi (blue curve) and of the bare PtSi substrate (black curve). The higher current density of IrO_2 can be attributed to the pseudocapacitive properties of IrO_2 . Both CV curves reported are acquired after 50 cycles of stabilization, with a scan rate of 50 mV·s⁻¹.

The CV curves reported in Figure 10 can be used to calculate the *CSC* by mean of Equation (3) [4,9]:

$$CSC = \frac{1}{v \cdot A} \int_{E_c}^{E_a} |i| dE \tag{3}$$

where E_a and E_c are the anodic and cathodic limits of the potential, *i* is the measured current, *v* is the scan rate, and *A* is the surface area of the electrode [4]. For ALD-prepared IrO₂, the value of *CSC* was calculated to be $1.9 \pm 0.1 \text{ mC} \cdot \text{cm}^{-2}$, while the bare PtSi substrate exhibited a *CSC* of $(2.4 \pm 0.2) \cdot 10^{-2} \text{ mC} \cdot \text{cm}^{-2}$. The value of *CSC* obtained for ALD-prepared IrO₂ is slightly lower compared to the non-activated sputtered IrO₂ reported in the literature (2.8 mC·cm⁻²) [3]. Nevertheless, a fair comparison should take into account the effective electrochemical surface area. IrO₂ deposited by reactive sputtering is generally characterized by higher surface roughness, while ALD-prepared thin films are generally smoother since they replicate the surface features of the underneath substrate conformally, as mentioned above in the AFM measurement paragraph.

To determine the maximum charge that the IrO₂ electrode can deliver without overcoming the cathodic limit for the water reduction, voltage transient (VT) measurements were performed. A current squared wave of different amplitudes was forwarded to the sample, recording the voltage (E_{we}) over time. The results reported in Figure 11 show the E_{we} as a function of time for values of current amplitude between 0.5 mA and 2.5 mA (Figure 11a). The maximum cathodic polarization (E_{mc}) was then calculated by the difference between the voltage peak (E_p) and the access voltage (E_a) [3]. Figure 11b shows the E_{mc} as a function of the charge injected. By linear regression of the data, it was possible to calculate that for $E_{mc} = -0.6$, the charge injected is 0.22 \pm 0.01 mC·cm⁻². Taking into account that the CIC is inversely proportional to the electrode's surface area [3], the value obtained can be considered as the lower boundary for ALD-prepared IrO_2 , in view of its application onto microelectrode arrays. We shall also note that CIC values higher than 1.0 mC·cm⁻² can be detrimental to neural stimulation because of possible neural damage [45].



Figure 11. Results of the voltage transient measurements performed on ALD-prepared IrO₂. (a) Shows the voltage of the working electrode (E_{we}) as function of time for squared current pulses of 0.5, 1.0, 1.5, 2.0, and 2.5 mA. (b) Reports the maximum polarization (E_{mc}), calculated by the difference between the peak voltage (E_p) and the access voltage (E_a), as function of the charge injected. By linear regression of the data (orange dashed line), it was possible to calculate the charge injection capacity to be 0.22 \pm 0.01 mC·cm⁻² for $E_{mc} = -0.6$.

4. Conclusions

In this work, we disclosed a novel PA-ALD process for the deposition of IrO_2 using (EtCp)Ir(CHD) as the precursor and a mix of Ar/O_2 plasma as the reactant. The growth characteristics, the physicochemical as well as the electrochemical properties of IrO_2 grown by PA-ALD were determined in view of the application in neuroelectronics. The use of the plasma allowed deposition at a relatively low temperature (150 °C), which can be helpful for the integration of the layer on existing devices as well as on flexible substrates. XRD results show the characteristic peaks of the metallic rutile-phase IrO_2 , indicating that the layer so prepared is nanocrystalline. TEM/EDS and ToF-SIMS analysis of ALD-prepared IrO_2 indicates that the layer is compact and continuous with low carbon contamination. TEM and AFM results highlight the conformality of the layer to the PtSi substrate. XPS results further confirm the presence of the metallic rutile phase of IrO_2 .

Electrochemical characterization showed that IrO₂ grown by PA-ALD has competitive performances for application in neuroelectronics. Specifically, EIS results revealed a strong capacitive coupling between the IrO₂ electrode and the electrolyte, with a C_{dl} of $301 \pm 4 \ \mu\text{F} \cdot \text{cm}^{-2}$, higher than the value reported in the literature for IrO₂ electrodeposited on Ti felt [42]. The value of C_{dl} obtained from CV was about $341 \pm 1 \ \mu\text{F} \cdot \text{cm}^{-2}$, in general agreement with the value determined with EIS, considering the different working principles of the two methods. To the best of our knowledge, the electrochemical characterization of the electrode/electrolyte interface in terms of charge injection capacity, charge storage capacity, and double-layer capacitance for IrO₂ grown by PA-ALD was not reported yet. Furthermore, the comparison between EIS and CV results for the determination of the double-layer capacitance is also an element of novelty in the field of neuroelectronics.

The CSC of IrO₂ was calculated in the range of -0.6-0.8 V vs. Ag | AgCl, where the oxidation and reduction reactions of water are negligible. The CSC value of 1.9 ± 0.1 mC·cm² is slightly lower than what is reported for non-activated electrodeposited IrO₂ (2.8 mC·cm²), although it should be considered that surface roughness has a big role in the electrochemical results. Finally, voltage transient measurements were performed in order to determine the maximum charge that the IrO₂ electrode can deliver without overcoming the cathodic limit

for the water reduction (-0.6 V). The charge injection capacity found for ALD-prepared IrO₂ was 0.22 ± 0.01 mC·cm⁻², in line with the literature [3]. The value obtained can be regarded as a lower limit in view of the integration of IrO₂ onto MEAs, since the charge injection capacity is inversely proportional to the surface area (1.0 cm² in this work) of the electrodes.

Supplementary Materials: The following supporting information can be downloaded at https: //www.mdpi.com/article/10.3390/nano13060976/s1. Equation (S1): RMS—root mean square roughness; Equation (S2): height–height correlation function; Equation (S3): gaussian fitting function; Figure S1: AFM of PtSi with the related height–height correlation function; Figure S2: power spectral density function (PSDF) spectra of all the AFM data on IrO₂ and PtSi; Figure S3: AFM measurement of IrO₂ deposited by PA-ALD onto Al_2O_3 (20 nm) on c-Si; Equation (S4): definition of the CPE impedance; Table S1: parameters of the equivalent circuit obtained from the modeling of the EIS data; Figure S4: plot of the capacitive current vs. scan rate obtained from CV measurements.

Author Contributions: Conceptualization, V.D.P. and M.F.; investigation, V.D.P., A.P., M.P., G.T. and D.C.; writing—original draft preparation, V.D.P., A.P., M.P., G.T., D.C. and M.F.; writing—review and editing, V.D.P. and M.F.; project administration, M.F.; funding acquisition, M.F. All authors have read and agreed to the published version of the manuscript.

Funding: This work has been supported by the European Commission (H2020-FETOPEN-2018-2019-2020-01, FET-Open project NEUREKA, GA-863245).

Data Availability Statement: The data presented in this work are available on request from the corresponding authors.

Acknowledgments: The authors thank Guilhem Larrieu, LAAS-CNRS, Université de Toulouse, CNRS, INP, Toulouse 31031, France, for providing the PtSi substrates.

Conflicts of Interest: The authors declare no conflict of interest.

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Article Ion-Induced Lateral Damage in the Focused Ion Beam Patterning of Topological Insulator Bi₂Se₃ Thin Films

Rubén Gracia-Abad ^{1,2,3,†}, Sandeep Kumar Chaluvadi ⁴, Pasquale Orgiani ⁴ and José María De Teresa ^{1,2,3,*,†}

- ¹ Instituto de Nanociencia y Materiales de Aragón (INMA), CSIC-Universidad de Zaragoza, 50009 Zaragoza, Spain
- ² Laboratorio de Microscopías Avanzadas (LMA), Universidad de Zaragoza, 50018 Zaragoza, Spain
- ³ Departamento de Física de la Materia Condensada, Universidad de Zaragoza, 50009 Zaragoza, Spain
- ⁴ CNR-IOM, TASC Laboratory in Area Science Park, 34149 Trieste, Italy
- * Correspondence: sangiao@unizar.es (S.S.); deteresa@unizar.es (J.M.D.T)
- † These authors contributed equally to this work.

Abstract: Focused Ion Beam patterning has become a widely applied technique in the last few decades in the micro- and nanofabrication of quantum materials, representing an important advantage in terms of resolution and versatility. However, ion irradiation can trigger undesired effects on the target material, most of them related to the damage created by the impinging ions that can severely affect the crystallinity of the sample, compromising the application of Focused Ion Beam to the fabrication of micro- and nanosized systems. We focus here on the case of Bi₂Se₃, a topological material whose unique properties rely on its crystallinity. In order to study the effects of ion irradiation on the structure of Bi₂Se₃, we irradiated with Ga⁺ ions the full width of Hall-bar devices made from thin films of this material, with the purpose of inducing changes in the electrical resistance and characterizing the damage created during the process. The results indicate that a relatively high ion dose is necessary to introduce significant changes in the conduction. This ion dose creates mediumrange lateral damage in the structure, manifested through the formation of an amorphous region that can extend laterally up to few hundreds of nanometers beyond the irradiated area. This amorphous material is no longer expected to behave as intrinsic Bi₂Se₃, indicating a spatial limitation for the devices fabricated through this technique.

Keywords: topological insulator; Bi2Se3; focused ion beam; patterning; irradiation damage

1. Introduction

During the last few decades, advances in miniaturization techniques, along with the requirements of size and shape of new devices, have allowed for probing the limits of the available lithography techniques. In particular, the use of Focused Ion Beam (FIB) has gained importance as a versatile technique that allows one to structure matter at the submicrometer scale, providing high control over the final shape and geometry of the devices [1]. This makes it ideal for the investigation of emerging materials in condensed matter, offering new possibilities for their manipulation and the investigation of unconventional behaviors [2].

The most straightforward application of FIB is direct milling [3,4]. In this process, the ions are accelerated and focused to a nanometric spot on a target sample, impinging on its surface. If the collisions are energetic enough, this enables material removal and patterning of extremely fine structures. However, FIB milling may induce uncontrollable damage coming from colliding ions, secondary processes, or heating effects. The consequences of these events depend on different factors, such as the target material or the working parameters, and the range of damage can go from a few tens to several hundred nanometers, considerably reducing the amount of functional material and significantly affecting the lateral resolution of the patterning. This can represent a serious limitation in

Citation: Gracia-Abad, R.; Sangiao, S.; Kumar Chaluvadi, S.; Orgiani, P.; Teresa, J.M.D. Ion-Induced Lateral Damage in the Focused Ion Beam Patterning of Topological Insulator Bi₂Se₃ Thin Films. *Materials* **2023**, *16*, 2244. https://doi.org/10.3390/ ma16062244

Academic Editor: Carles Corbella Roca

Received: 21 February 2023 Revised: 3 March 2023 Accepted: 8 March 2023 Published: 10 March 2023



Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). certain cases [5]. In addition, in nanosystems, the range of damage can be comparable to the size of the system, significantly altering their properties [6]. On the other hand, in many materials, preserving the properties of their surfaces is crucial so that they show their most intriguing characteristics.

Nowadays, topological materials are a hot topic in the field of condensed matter physics. Specifically, topological insulators (TI) have attracted much attention due to their potential application in quantum computing and spintronics [7]. These materials behave as insulators in their interior, whereas they support topologically protected metallic surface states. Notably, Bi₂Se₃ is one of the most studied TIs due to its simple surface band structure, containing a single Dirac cone, and its relatively large bandgap that should make the topological regime in which the bulk states are suppressed more accessible [8].

Several techniques have been applied for the patterning of Bi₂Se₃ thin films so far, UV lithography being the most widely used [9–11]. Regarding the fabrication of contacts, Electron Beam Lithography (EBL) has also been employed [12,13], avoiding the use of masks present in UV lithography, and simplifying the process. However, both require the use of chemical resists and multiple steps [14]. In this sense, FIB patterning represents an advantage since it is resist-free, which avoids possible chemical contamination or degradation of the surface. Besides, it can be implemented in a single quick step, and it offers the ability to customize the final design [2]. Nevertheless, the unique properties of this material are highly dependent on its crystallinity as well as on the quality of the interfaces, and these factors can be altered by ion irradiation. This is the reason why a deep understanding of such effects is necessary. FIB patterning has already been applied on Bi₂Se₃ for the fabrication of nanowires [15,16] and even damage has been considered in some studies [17]. Here, the authors demonstrated the good capabilities of FIB for shaping and thinning Bi₂Se₃ flakes, and they also reported the creation of amorphous regions in the material, as well as the formation of Se-deficient areas, that can also affect transport. All these effects established a limitation for the fabrication of high-quality nanowires down to a width of 150 nm. However, a systematic analysis of FIB-induced damage in Bi₂Se₃ thin films with different thicknesses showing a detailed structure characterization of that damage is lacking.

Herein, we investigate the effects of using FIB on Bi₂Se₃ thin films in order to establish the possible limitations of this technique. We first irradiate Hall-bar systems made out of Bi₂Se₃ films and check how their electrical resistance changes. Subsequently, the effects produced on the crystal structure are characterized. We will show that the damage presents a medium-range character, extending laterally up to several hundred nanometers beyond the point of impact. Such an undesired effect should be taken into account when fabricating Bi₂Se₃-based devices at the submicrometer scale by FIB.

2. Materials and Methods

For the purpose of this work, several 4 μ m-wide Hall-bar devices were prepared by optical lithography from Bi₂Se₃ thin films of 12.5, 40, 45, 52, and 55 nm thickness (information for the 45 nm sample is used in the Supplementary File) [18–20]. The films were grown by Pulsed Laser Deposition (PLD) on sapphire (001) substrates. Their crystallinity was characterized by X-ray Diffraction (XRD), whereas the presence of topological surface states was validated by Angle-Resolved Photoemission Spectroscopy (ARPES). The lithography process was carried out in an MA6 mask-aligner from SUSS MICROTEC (Garching bei München, Germany) following a two-step process, with a first standard etching process to define the Hall bar, and a second lift-off process in order to define the electrical contacts. For the etching, an ion milling machine model 600 from SISTEC (Chemnitz, Germany) was used, whereas an Auto500 e-beam evaporator from BOC Edwards (Burgess Hill, UK) was employed for the growth of the gold contacts.

The electrical properties of the films were characterized by magnetotransport measurements in a Physical Properties Measurement System (PPMS) from Quantum Design (San Diego, CA, USA), covering temperatures down to 2 K and perpendicular magnetic fields up to 9 T. The longitudinal resistivity versus temperature curve shows a metallic behavior (Figure 1a), whereas the magnetic dependence of the Hall resistivity determines that the transport is n-type and is attributed to a single type of carrier (Figure 1b). This has been previously reported in pure Bi₂Se₃ and is ascribed to the natural formation of Se vacancies in the material that act as donor impurities, populating the bulk conduction band, and hindering the isolation of the topological surface states. Hall resistivity measurements allow us to determine a sheet carrier density and a mobility in the range of $(1.8-31.5) \cdot 10^{13}$ cm⁻² and 50.3–77.5 cm²/(V · s), respectively, indicating a strong contribution to transport from the bulk states in these samples [21–23].



Figure 1. Electrical measurements of Bi_2Se_3 samples with thicknesses of 12.5, 40, and 55 nm: (a) Thermal dependence of the longitudinal resistivity. (b) Magnetic field dependence of the Hall resistivity measured at 2 K.

The Hall bars were irradiated across their full width using line patterns. Each irradiation process was carried out in a working region, which is defined as the region in the Hall bar between two consecutive contacts. Inside the region, a series of lines made with an increasing ion dose are performed in order to induce changes in its electrical resistance (see Figures 2 and 3), looking for the minimum dose necessary to produce significant changes in the electrical response of the system. For the irradiation process, a Dual Beam Helios Nanolab 650 FIB-SEM equipment from Thermofisher (Hillsboro, OR, USA) was used. This equipment combines a vertical field-emission electron column with a 52° tilted Ga-based ion column, both with a maximum acceleration voltage of 30 kV, which allows one to simultaneously fabricate and image the process. Both beams intersect at the eucentric point, which is placed 4.15 mm below the pole of the electron column. The accelerating voltage and current of the ion column were 30 kV and 1.1 pA, respectively. A dwell time of 1 μ s and a beam spot overlap of 50% were chosen. The ion dose was progressively increased by simply increasing the irradiation time.

Electrical resistance was extracted from I-V curves taken in situ after each irradiation line pattern, using electrical microprobes from Kleindiek Nanotechnik GmbH (Reutlingen, Germany) and a 6221 DC current source/2182A nanovoltmeter from Keithley Instruments (Cleveland, OH, USA), with a two-probe measurement configuration by injecting a DC current and measuring the voltage drop simultaneously (Figure 3a). Contact resistance was negligible in this case (order of magnitude of few Ω) compared to device resistance (order of magnitude of few k Ω), and since we are interested in resistance changes and not in absolute values of the resistance, four-probe measurements were not required.

For structural characterization, some lamellas of the irradiated regions were prepared and observed in a Titan Cube Transmission Electron Microscope from Thermofisher (Hillsboro, OR, USA) with High-Resolution Transmission Electron Microscopy (HRTEM) capabilities. This equipment provides atomic resolution of the lattice structure, enabling examination of the structural effects caused by ion irradiation in the sample and the determination of the extent of damage.



Figure 2. Sketch of the irradiation process of a working region. The white arrow indicates the sense of increasing irradiation dose, as indicated below in Figure 3b.



Figure 3. Scanning Electron Microscopy (SEM) images showing: (**a**) microprobes configuration for the in situ electrical measurements. (**b**) Magnified view of the region marked with a red rectangle in (**a**). FIB-irradiated line patterns through the entire width in a working region of a Hall-bar device. The dashed white arrow indicates the sense of increasing ion dose.

3. Results

Figure 4 shows the evolution of the change in electrical resistance against the gallium ion dose for the four different film thicknesses. The change in resistance $R - R_i$ for a given dose is calculated as the difference between the resistance after (R) and before (R_i) irradiating a line with that dose. In this way, the increment due only to the last irradiation is obtained. Ion dose is expressed in both ion/cm and in ion/cm². For the latter, a beam spot size of 7 nm provided by the chosen working parameters was considered. For all samples the same behavior was observed: first, a nearly flat region in which the resistance increased slightly. For this range of relatively low doses, only localized amorphization of the structural lattice took place (see the Supplementary File for more details on the evolution of the damage with increasing ion dose). After a certain value of the ion dose, milling started and the amorphization spread beyond the irradiated area. However, no significant changes in the resistance were observed until a higher dose was applied, at which it increased sharply. After this abrupt increase, the electrical resistance increased several orders of magnitude, and the sample could be considered electrically insulating. Thus, the irradiation produces an insulating region in the bar.



Figure 4. Change in electrical resistance $R - R_i$, calculated as the difference between the resistance after (*R*) and before (*R_i*) irradiating a line with a given dose value (*D*), as a function of the ion dose for samples with four different thicknesses: 12.5 (a), 40 (b), 52 (c), and 55 nm (d). In the lower x-axis, the dose is expressed in ion/cm, whereas in the upper one, it is expressed in ion/cm², considering the beam spot diameter. The insets show the low ion dose region in more detail.

In order to compare this feature among the different samples, we can establish a criterion according to which the sample can be considered electrically cut off. This is made to correspond to a value of change of 20 times the initial electrical resistance R_0 . The dose corresponding to the irradiation producing such a change is called the critical dose D_c . The values of D_c extracted through this criterion are shown in Table 1. As expected, D_c increases with increasing thickness. The value of the present doses is in good agreement with the one found in previous work [16], where an ~8 nm Bi₂Se₃ film with a 20 nm to 30 nm capping layer of Se was irradiated, showing an abrupt increase of the electrical resistance at $3.6 \cdot 10^{16}$ ion/cm².

Table 1. Values of D_c for different thicknesses in ion/cm and ion/cm².

<i>t</i> (nm)	$D_c \ (10^{10} \ \text{ion/cm})$	$D_c (10^{16} \text{ ion/cm}^2)$
12.5	3.0 ± 0.9	4.2 ± 0.8
40	12.2 ± 1.0	17.2 ± 0.9
52	13.5 ± 0.2	19.3 ± 0.2
55	15.5 ± 1.9	21.0 ± 1.6

To closely examine the effects of the FIB-irradiation process on the samples and to correlate the behavior of the electrical resistance against ion dose with the formation of damage in the crystalline structure, several lamellas corresponding to different doses and thicknesses were prepared and studied by HRTEM (see the Supplementary File for additional images on structural characterization). First, Figure 5 shows the effects of irradiation on three of the four thicknesses for a dose value around D_c , demonstrating severe lateral damage, reaching from tens of nanometers in the 12.5 nm-thick sample (Figure 5a) up to several hundred nanometers in the 55 nm-thick sample (Figure 5c). In all cases, medium-range damage (>t) was observed. This could represent a limitation when applying FIB fabrication to this material, significantly reducing the amount of functional material and representing a constraint for the lateral size of the device. It can be observed that whereas in the thinnest film the damage covers the entire thickness of the film, in the thicker ones, the damage takes place just at the region closest to the film surface. In general, an increase in the range of damage was found with increasing thickness, as expected from the higher dose required for the corresponding irradiation processes.



Figure 5. Transmission Electron Microscopy (TEM) images, with white double-headed arrows showing the damage range after high dose irradiation in samples with thicknesses: (**a**) 12.5 nm, (**b**) 40 nm, and (**c**) 55 nm. In (**a**,**b**), just one side of the irradiated zone is shown, whereas in (**c**), both are presented.

Regarding the nature of the damage, amorphization took place in the majority of the region. However, this was not happening throughout the affected structure. It was observed in different irradiated areas that right next to the irradiated region, a small area of polycrystalline material was formed. This can be attributed to recrystallization of the region closest to the irradiated area due to local heating that arises from the energy transfer of the ions to the crystal lattice [24,25]. The damage extended throughout the lateral dimension, but in the region closest to the beam incidence point, the temperature was high enough to produce partial recrystallization. The differences in structure can be further confirmed by taking the Fast Fourier Transforms (FFT) of the structure in the TEM images (See Figure S7 in Supplementary File).

As a summary of the observed results, a plot with the values of D_c and the lateral damage range against the thickness of the sample is presented in Figure 6. This shows that D_c scales almost linearly with thickness. A slight deviation from linearity might be expected due to several factors that participate in the interaction of the ions with the sample, such as local heating or backscattering produced by the substrate, which makes the

process more difficult to describe. Indeed, local heating acts as a source of recrystallization. Grain formation after recrystallization might even favor electrical transport through the amorphized areas, delaying the electrical cut. The linear trend was not observed in lateral damage, but a relatively large damage (>t) was found in the thinner film of 12.5 nm. In this case, the sapphire substrate can act as a strong source of backscattering that plays an important role in the lateral spreading of the damage. For thicker films, the substrate is not expected to play such a relevant role at the beginning of the irradiation process, given that the ion dose reaching the substrate is much lower. Theoretical or simulation results would be necessary for a more comprehensive understanding of all the complex physical processes involved in the ion irradiation of Bi₂Se₃ films.



Figure 6. Critical dose D_c with linear fitting and lateral damage range plotted against thickness.

4. Conclusions and Outlook

We have fabricated and ion irradiated Bi₂Se₃ patterned films of different thicknesses in order to study the effects of ion irradiation on their electrical resistance and on their crystalline structure. The evolution of the electrical resistance with the increase in ion dose showed initially a weak effect. Only after exceeding a given dose, the electrical resistance changed significantly. This corresponded to the formation of an insulating trench.

In addition, the structural characterization by TEM allowed us to study the range of damage created by the impinging ions. We observed a first stage in which only amorphization took place, remaining localized, followed by a second stage in which milling was triggered, leading to a lateral spreading of the amorphization in the crystalline structure up to several hundred nanometers beyond the irradiated area. This study was carried out under soft working conditions, given that the Ga beam current was set to 1.1 pA, which can be considered a low current corresponding to a short tail in the beam profile.

With these results in mind, we can conclude that there are spatial limitations when directly applying FIB to the fabrication of Bi_2Se_3 devices. Specifically, when fabricating devices with dimensions comparable to the extent of the damage, the final performance of the device could be seriously affected. This consideration becomes even more important in thinner samples, where the damage might spread down to the substrate for the entire affected region. Some routes for reducing the damage created by ions have considered the idea of annealing at temperatures around 300 °C [26]. In other cases, the functional thin films are protected with a sacrificial layer [27]. Other studies have shown that decreasing substrate temperature below room temperature can considerably reduce the amount of damage caused by ion irradiation [5,28,29], which can be an interesting route for further research.

Supplementary Materials: The following supporting information can be downloaded at: https: //www.mdpi.com/article/10.3390/ma16062244/s1, Figure S1: Evolution of structural damage with increasing ion dose, Figure S2: Evolution of the I–V characteristics with increasing ion dose, Figure S3: Additional Transmission Electron Microscopy images for the 12.5 nm-thick sample, Figure S4: Additional Transmission Electron Microscopy images for the 40 nm-thick sample, Figure S5: Transmission Electron Microscopy images for the 52 nm-thick sample, Figure S6: Additional Transmission Electron Microscopy images for the 55 nm-thick sample, Figure S7: Transmission Electron Microscopy image with Fast Fourier Transforms of damaged regions. Reference [30] is cited in the Supplementary File.

Author Contributions: Investigation, writing—original draft preparation, R.G.-A.; writing—review, editing, and visualization, R.G.-A., S.S. and J.M.D.T.; supervision, S.S. and J.M.D.T.; conceptualization and funding acquisition, J.M.D.T.; resources, S.K.C. and P.O. All authors have read and agreed to the published version of the manuscript.

Funding: The financial support of the Gobierno de Aragón is acknowledged through a doctoral fellowship (R.G.A) and through the grant E13-20R, with European Social Funds (Construyendo Europa desde Aragón). The authors acknowledge support from networks COST FIT4NANO and CSIC Research Platform PTI-001, and from MCIN/AEI/10.13039/501100011033 through the grant PID2020-112914RB-I00.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The data are available under reasonable request.

Acknowledgments: We acknowledge Gerhard Hobler for the helpful discussions of the results.

Conflicts of Interest: The authors declare no conflict of interest.

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Ahmad M. Alsaad ^{1,*}, Qais M. Al-Bataineh ^{1,2}, Issam A. Qattan ^{3,*}, Ihsan A. Aljarrah ¹, Areen A. Bani-Salameh ¹, Ahmad A. Ahmad ¹, Borhan A. Albiss ¹, Ahmad Telfah ^{2,4} and Renat F. Sabirianov ⁵

- ¹ Department of Physics, Jordan University of Science & Technology, P.O. Box 3030, Irbid 22110, Jordan
- ² Leibniz Institut für Analytische Wissenschaften-ISAS-e.V., Bunsen-Kirchhoff-Straße 11, 44139 Dortmund, Germany
- ³ Department of Physics, Khalifa University of Science and Technology, Abu Dhabi P.O. Box 127788, United Arab Emirates
- ⁴ Nanotechnology Center for Scientific Research, The University of Jordan, Amman 11942, Jordan
- ⁵ Department of Physics, University of Nebraska at Omaha, Omaha, NE 68182, USA
- * Correspondence: alsaad11@just.edu.jo (A.M.A.); issam.qattan@ku.ac.ae (I.A.Q.)

Abstract: We fabricated ferroelectric films of the organic molecular diisopropylammonium chloride (DIPAC) using the dip-coating technique and characterized their properties using various methods. Fourier-transform infrared, scanning electron microscopy, and X-ray diffraction analysis revealed the structural features of the films. We also performed ab-initio calculations to investigate the electronic and polar properties of the DIPAC crystal, which were found to be consistent with the experimental results. In particular, the optical band gap of the DIPAC crystal was estimated to be around 4.5 eV from the band structure total density-of-states obtained by HSE06 hybrid functional methods, in good agreement with the value derived from the Tauc plot analysis ($4.05 \pm 0.16 \text{ eV}$). The films displayed an island-like morphology on the surface and showed increasing electrical conductivity with temperature, with a calculated thermal activation energy of 2.24 \pm 0.03 eV. Our findings suggest that DIPAC films could be a promising alternative to lead-based perovskites for various applications such as piezoelectric devices, optoelectronics, sensors, data storage, and microelectromechanical systems.

Keywords: diisopropylammonium chloride (DIPAC) structural; optical; electrical; FTIR; SEM; electric polarization; ab initio calculations

1. Introduction

Recently, molecular ferroelectrics have emerged as a promising alternative to traditional inorganic ferroelectrics due to several advantageous properties, such as multifunctionality, low density, low cost, and solution processability. These properties make them potential candidates for the development of all-organic electronic devices. Ferroelectric compounds are characterized by exhibiting ferroelectric-paraelectric phase transitions. Such transitions occur at critical temperatures (T_c) [1]. Conventional inorganic polar crystals such as lead zirconate titanate and barium titanate have been used for decades, owing to their extraordinary ferroelectric properties. However, because of their toxicity effects on the environment and hard processing in addition to their heavyweight, manufactured molecular ferroelectric crystals attract more attention due to their appealing and brilliant properties, such as being lightweight, easy to process, and environmentally friendly [2,3]. However, the practical applications of molecular ferroelectrics have been limited due to their relatively low melting and Curie temperatures, as well as their small spontaneous polarization. To address these limitations, recent studies have investigated the ferroelectric properties of diisopropylammonium halide (DIPAX, X = Cl, Br) molecular crystal systems, which have demonstrated enhanced ferroelectricity [4-6].

Citation: Alsaad, A.M.; Al-Bataineh, Q.M.; Qattan, I.A.; Aljarrah, I.A.; Bani-Salameh, A.A.; Ahmad, A.A.; Albiss, B.A.; Telfah, A.; Sabirianov, R.F. Physicochemical Properties of Organic Molecular Ferroelectric Diisopropylammonium Chloride Thin Films. *Nanomaterials* **2023**, *13*, 1200. https://doi.org/10.3390/ nano13071200

Academic Editors: Ricardo Lopez Anton, Jose Maria De Teresa and Sion Federico Olive Méndez

Received: 2 March 2023 Revised: 13 March 2023 Accepted: 14 March 2023 Published: 28 March 2023



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As a ferroelectric material, DIPAC has a strong tendency for polarization switching, enabling it to be employed for several applications, such as nonlinear capacitors, pyroelectric, data storage, and electro-optical devices [7,8]. DIPAC has been reported to be an inexpensive and easy-to = prepare organic salt with Curie temperature ($T_c = 440$ K) [9–17]. It exhibits a large spontaneous polarization (P_s) of about 8.9 µC/cm². This value is extremely large compared to those of poly(vinylidene difluoride) (PVDF, $\approx 8 \mu$ C/cm²) and Nylon-11 ($\approx 5 \mu$ C·cm²).

In a previous study, we conducted both computational and experimental investigations of the structural, optical, electronic, crystallographic, and physical properties of thin films composed of diisopropylammonium bromide ($C_6H_{16}BrN$, DIPAB). Ab initio simulations were also implemented to calculate the key structural parameters. as well as the bandgap energy of DIPAB. The measured and calculated electronic and optical properties of the DIPAB thin films reveal a fairly good agreement between the measured and calculated parameters [1]. In addition, the optical properties of synthesized DIPAB thin films were measured and interpreted. The study was the first of its kind. Previous works were geared toward investigating and interpreting the interplay between the electrical and dielectric properties of DIPAB films. The significance of investigating the optical properties of thin films composed of diisopropylammonium halides (DIPAX, X = Br, Cl) lies in their potential use in a range of applications, including optical lenses, display panels, and solar cells [18].

Few attempts to grow thin-film-based DIPAX (X: F, Cl, Br, and I) have been made on surfaces and typically end up with the formation of randomly distributed microcrystals [19,20]. A way to extend the application of these materials in devices is to control their spontaneous tendency to crystallize in order to obtain homogeneous thin films [21]. The main objective of this study is to optimize the optical and electrical properties of ferroelectric thin films made from diisopropylammonium chloride (DIPAC) that are both cost-effective and high-performing. Successful optimization of these key parameters ensures the scaled fabrication of multifunctional optoelectronic devices that are low cost and that operate more effectively than current devices. In particular, we focus on investigating and interpreting the structural, optical, electronic, crystallographic, and physical properties through experimental means. By doing so, we aim at monitoring the potential characteristics of these materials.

In parallel, first-principle simulations were conducted to mimic DIPAC thin films to support the experimental investigations [1]. DIPAC has attracted the attention of researchers as a novel organic ferroelectric material. owing to its promising ferroelectric characteristics such as high spontaneous polarization ($P_s \approx 8.9 \,\mu\text{C/cm}^2$) at room temperature and high-density organic ferroelectric RAM (FeRAM). It exhibits extremely high Curie temperatures ($T_c = 440 \text{ K}$) [5,7]. Therefore, fabricating high-density FeRAM based on ferroelectric DIPAC thin films becomes possible. DIPAC has been extensively investigated for its promising ferroelectric characteristics using various techniques, such as dielectric spectroscopy and X-ray diffraction, to analyze its electrical and structural properties [22–25]. In this study, we focus on the optical properties of DIPAC thin films as potential candidates for the development of multifunctional scaled optoelectronic devices.

2. Experiments and Calculations

The main ingredient used to prepare DIPAC thin films is diisopropylammonium (DIPA) ($C_6H_{16}N$; Mw = 102.20 g/mol) that was purchased from AK Scientific (Union City, CA, USA). Other materials such as hydrochloric acid (HCl; Mw = 36.46 g/mol) and 12-Crown-4 ($C_8H_{16}O_4$) (Mw = 176.21 g/mol) were purchased from Sigma-Aldrich (Darmstadt, Germany). To prepare the DIPAC ($C_6H_{16}NCl$) solution, 0.999 mL of diisopropylammonium cation and 0.001 mL of hydrochloric acid anion were variegated in 100 mL absolute ethanol in a 1:1 molar ratio by utilizing slow evaporation with continuous magnetic stirring at room temperature. The stabilizer (0.01 mL of 12-crown-4) was then added to the solution while maintaining continuous stirring for 1 h at room temperature. The synthesized DIPAC thin film was coated on a fused silica glass substrate using a dip coating technique for 2 h. The

entire mixture was then dried at 40 °C overnight under normal air atmospheric pressure. The thickness of the film was calculated to be about 250 ± 20 nm, using the mathematical model of Al Bataineh et al. [26].

The Fourier transform infrared spectroscopy (FTIR) spectra of the synthesized DIPAC crystalline thin films were obtained using a Bruker Tensor 27 spectrometer (Karlsruhe, Germany) in the spectral range of 4000–400 cm⁻¹. Crystalline properties of as-prepared thin films were investigated by measuring X-ray diffraction (XRD) patterns. The patterns were accurately measured by employing a Malvern Panalytical Ltd. (Malvern, UK) diffractometer facility at room temperature with CuK α radiation (0.1540598 nm). The incident angles were varied from 30° to 60° with a step of 0.02° and an energy resolution of 20%. The main objective of the current work was geared toward optimizing the optical and electrical properties of DIPAC thin films.

To elucidate a deeper understanding of the optical properties of the synthesized DIPAC thin films, a UV–Vis spectrophotometer (Hitachi U-3900H, Tokyo, Japan) was utilized to measure the UV–Vis spectra in the 250–700 nm spectral range. Electrical properties were crucial in our investigations of this novel material. The 2D electrical conductivity sheets were obtained at room temperature using a 4-point probe (Microworld Inc., New Jersey, USA) equipped with a high-resolution multimeter (Keithley 2450 Sourcemeter, Beaverton, OR, USA).

To comprehensively deepen the understanding of the structural and physical properties of DIPAC films, ab initio simulations within the framework of the density functional theory [27,28] were utilized to conduct a detailed investigation of DIPAC. The electronic structure was computed by employing the projector augmented wave (PAW) method [29], as implemented in the Vienna ab initio simulation package (VASP) [30]. The Perdew–Burke– Ernzerhof (PBE) exchange-correlation form of the generalized gradient approximation (GGA) [31,32] was implemented to model the layered DIPAC molecule. Moreover, a hybrid functional method [33] based on the Fock exchange in real space was introduced to designate a broad range of molecular properties. The HSE06 hybrid functional method was applied to determine the electronic properties of the polar DIPAC crystal [34,35]. The key parameters, such as optical bandgap, were determined using the HSE06 hybrid functional method. This method was anticipated to yield a more accurate band gap of DIPAC than the values previously reported using the GGA approach (an approach that was proven to underestimate the value of the bandgap).

It is worth mentioning that the samples prepared in this work can be easily reproducible. The materials used to prepare samples are easily available and can be purchased immediately. The synthesis technique used to prepare samples is straightforward. Indeed, all samples of different sizes and features were reproduced several times. The characterization techniques of the samples employed in this work have shown that different samples yield the same results. Since the samples were subjected to same preparation conditions, the obtained results on different samples were statically the same. This was an adequate indication that the samples were reproducible. Moreover, the materials used, the preparation techniques employed, and the characterization methods utilized were inexpensive and easy to perform.

3. Results and Discussion

3.1. Chemical Properties

The chemical structure of DIPAC is mainly composed of DIPA molecules bonded together via chloride ions. It exhibits a large value of spontaneous polarization around $P_s \sim 8.82 \ \mu C \cdot cm^{-2}$ [4]. The FTIR spectra of the DIPAC film (Figure 1) were investigated to study the nature of the interaction between DIPA and chloride ions. The vibrational bands between 2400–3000 cm⁻¹ were assigned to N–H stretching vibrations, while the vibrational band at 2095 cm⁻¹ was associated with N–H bending vibrations. The -CH₃ stretching bands appeared at 1585 cm⁻¹, while the C–N and C–O stretching bands were located in the 1250–1400 cm⁻¹ and 1000–1200 cm⁻¹ spectral ranges. The C–Cl stretching

band was the main vibrational band that determined the interaction between the DIPA and Cl and appeared in the $500-1000 \text{ cm}^{-1}$ spectral range.



Figure 1. The FTIR spectrum of DIPAC.

3.2. Crystal Structure and Morphological Properties

The XRD pattern (Figure 2) of DIPAC film exhibits peaked at 12.24°, 16.78°, 22.46°, 25.04°, 27.42°, 31.98°, and 32.86°, corresponding to DIPAC crystallographic planes indexed by Miller indices ((001), (110), (020), (002), (012), (201), and (300), respectively). The obtained XRD pattern clearly indicated the polycrystalline monoclinic structure of DIPAC molecule.



Figure 2. The XRD patterns of the DIPAC thin films.

The monoclinic structure of the DIPAC molecular crystal was also determined by DFT-based calculations, with lattice constants of a = 7.495 Å, b = 7.818 Å and c = 7.655 Å,

 $\alpha^{\circ} = \gamma^{\circ} = 90^{\circ}$ and $\beta^{\circ} = 114.640^{\circ}$ (Table 1, Figure 3). The lattice constants and angle β° were calculated using the following formula:

$$\frac{1}{d^2} = \frac{1}{\sin^2 \beta} \left(\frac{h^2}{a^2} + \frac{k^2 \sin^2 \beta}{b^2} + \frac{l^2}{c^2} - \frac{2h \log \beta}{ac} \right)$$
(1)

Table 1. The structural properties of polar monoclinic phase of DIPAC molecular crystal.

DFT	Exp.	
C ₆ H ₁₆ Cl N	C ₆ H ₁₆ Cl N	
8.90	-	
Monoclinic	Monoclinic	
P21	P21	
7.495	7.239	
7.818	7.901	
7.655	7.397	
90	90	
114.640	114.870	
90	90	
_	10	
_	0.0095	
	DFT C ₆ H ₁₆ Cl N 8.90 Monoclinic P2 ₁ 7.495 7.818 7.655 90 114.640 90 - -	$\begin{array}{ c c c c } \hline DFT & Exp. \\ \hline C_6 H_{16} Cl N & C_6 H_{16} Cl N \\ 8.90 & - \\ \hline Monoclinic & Monoclinic \\ P2_1 & P2_1 \\ 7.495 & 7.239 \\ 7.818 & 7.901 \\ 7.655 & 7.397 \\ 90 & 90 \\ 114.640 & 114.870 \\ 90 & 90 \\ - & 10 \\ - & 0.0095 \\ \hline \end{array}$



Figure 3. A schematic diagram of the DIPAC polar crystal.

The lattice constants (*a*, *b*, and *c*) of the monoclinic DIPAC molecular crystal were determined using the formula presented, where *d* represents planar spacing and was computed using Bragg's law with X-ray wavelength λ (0.1540598 nm) and incidence angle θ . The values of the lattice constants of the DIPAC film were calculated and tabulated, as shown in Table 1. The results obtained through DFT calculations were compared to the XRD experimental outcomes, as presented in Figure 2, indicating good agreement.

The crystallite size (*D*) and lattice strain $\langle \varepsilon \rangle$ were calculated by employing the Williamson– Hall (W–H) method modified by the uniform deformation model (UDM), according to the previous literature [33]. The estimated values of the crystallite size *D* and the microstrain $\langle \varepsilon \rangle$ of DIPAC film were tabulated, as shown in Table 1.

As shown in Figure 4, SEM micrographs were taken at 50, 10, and 1 μ m enlargement scales to observe the surface of DIPAC film. It was found that the film had cracks that were distributed in an island-like pattern. The cracks on the surface provided paths for the penetration of chlorides into DIPA molecules, which led to the reinforcement of chloride-induced island-like patterns. The morphology of the elongated microcrystals was observed to be island-shaped with a common orientation over a large area for all enlargement scales. The width and height distributions of the microcrystals were greatly influenced by growth conditions. The size of the single unit was approximately 100 nm. Additionally, the



short-scale micrograph (1 μ m) indicated that the coarse units of the cracks also exhibited a micro-sheet-like pattern.

Figure 4. The SEM micrographs of DIPAC film at different enlargement scales (a) 50, (b) 10, and (c) 1 µm.

3.3. Optical Properties

The optical properties of DIPAC film were examined using a UV-Vis spectrophotometer at room temperature within the spectral range of 250–700 nm. The transmittance spectra showed a rapid increase in values from 0 to 90% as the incident photon wavelength increased from 300 nm to 370 nm, with negligible change in values as the wavelength increased from 370 nm to 700 nm (Figure 5a). The decrease in the transmittance spectra below the absorption edge can be attributed to the interband transition. The band gap energy was determined using Tauc plot [34] and found to be 4.05 \pm 0.16 eV (inset of Figure 5a).



Figure 5. (a) Transmittance, (b) refractive index, and (c) extinction coefficient of DIPAC film. The inset in (a) represents the Tauc plot of DIPAC film.

The refractive index and extinction coefficient were calculated using transmittance and reflectance spectra, based on previous literature [26,35]. The refractive index exhibited normal dispersion in the (350–700) nm spectral region, with a continuous decrease in values from 1.88 to 1.54 as the wavelength of the incident photon increased (Figure 5b); the refractive index spectra of DIPAC film was affected with the cracks behavior. In addition, the spectral region of (250–350) nm showed anomalous dispersion, due to the resonance phenomenon, occurring when the frequency of the incident photon matched the plasma frequency of the vibrating electric dipoles. The extinction coefficient showed a decrease in the high energy region (300–350) nm and vanished for wavelengths greater than 400 nm, indicating that the DIPAC film was transparent in the visible region (Figure 5c).

3.4. Electric Polarization of DIPAC

The Berry phase quantum mechanical approach was used to describe the macroscopic polarization of DIPAC [28,29,36–38], and the difference in total polarization between two

phases was the spontaneous polarization P_s . The equilibrium lattice parameters were slightly reduced by performing the Van der Waals correction to energy using the DFT-D3 method with Becke–Jonson damping in VASP [39,40]. According to the calculations, the spontaneous polarization of α -DIPAC was $P_s = 8.82 \,\mu\text{C/cm}^2$, which was consistent with previous theoretical results [41].

DIPAC has the highest T_c among known molecular ferroelectrics ($T_c = 440$ K). These values of P_s and T_c suggest that DIPAC has the potential to be used in high-temperature piezoelectric and optoelectronic devices. The energy difference between the polar and paraelectric phase is 12.5 eV, which can be used to determine the Curie temperature of DIPAC crystal [42,43]. The ferroelectric–paraelectric phase transition occurs at 440 K, which is well above room temperature, making DIPAC an excellent alternative to perovskites for high-temperature device applications [44].

The electrical conductivity of the DIPAC film was measured using a 4-point probe at various temperatures ranging from 300 K to 323 K. A conductivity mapping of the DIPAC film (Figure 6a) indicated that the film had a low conductivity with a non-significant distribution, averaging 3.6 μ S/cm. The average electrical conductivities (σ) for temperatures 300 K, 308 K, 313 K, 318 K, and 323 K were plotted against (1000/T(K)), as shown in Figure 6b, and fitted to the Arrhenius formula. The Arrhenius-like behavior of σ is described as $\sigma = \sigma_0 \exp(-E_a/K_BT)$, where σ_0 is the pre-exponential factor, *T* is the temperature [K], *K*_B stands for the Boltzmann constant, and *E*_a is the activation energy [45]. The *E*_a parameter was deduced from the electrical conductivity was found to be 2.24 \pm 0.03 eV. The perfect fit indicated that the system is thermally activated. This behavior can be directly related to the significant surge of the cations' *E*_a value, leading to the cation jump to the next coordinating site and, thus, increasing the energy of segment vibrations [46] which, in turn, leads to abrupt segmental motion counter to the hydrostatic pressure [47]. In addition, increasing the temperature enhances a significant carrier concentration mobility of the free electrons [46,48].



Figure 6. (a) The conductivity mapping $(1 \text{ cm} \times 1 \text{ cm})$ of DIPAC thin film, (b) electrical conductivity of DIPAC films as a function of 1000/T [K⁻¹].

3.5. Electronic Properties

We optimized the lattice parameters of DIPAC using a total energy minimization approach and followed the Hellmann–Feynman (HF) forces on the ionic sites in the unit cell of DIPAC. The HF forces were minimized to be as small as 0.002 eV/Å. We calculated other key parameters, such as the density of states (DOS) and the band structure of DIPAC. The electronic band structure of polar DIPAC was computed using the HSE06 method, as demonstrated in (Figure 7a). The calculated bandgap energy was found to be approximately 4.5 eV, indicating that polar DIPAC is a wide-bandgap insulator. The DOS and partial DOS (PDOS) of DIPAC were also calculated using the HSE06 method (Figure 7b). The PDOS plots indicated that the valence band consists mainly of Cl (p) orbitals, while the conduction band is dominant by C(p), C(s), N(p), and N(s) states. This confirms the fact that the interband transitions mainly occurred from the valence bands of Cl atoms to the conduction bands of C and N atoms in the DIPAC molecule.



Figure 7. (a) The electronic energy band structure, and (b) the DOSs and PDOSs of DIPAC.

4. Conclusions

In conclusion, as-synthesized DIPAC thin films are primarily composed of DIPA molecules that are interconnected through chloride ions, as revealed by XRD as well as by FTIR measurements. The measured optical bandgap value of DIPAC films indicated that it behaves as an insulator and exhibits excellent dielectric properties. We obtained high-transmittance value in the 300-700 nm spectral range in the DIPAC film. DIPAC exhibited a wide optical bandgap of 4.5 eV. Increasing the temperature enhanced the available free volume around the DIPAC chains significantly. Consequently, higher ion mobility and thermally activated electrical conductivity of DIPAC films were observed in this work. Using the Berry Phase Approach (BPA), polar DIPAC was found to exhibit a ferroelectric phase transition temperature of 440 K with a large value of spontaneous polarization of 8.82 μ C/cm². This spontaneous polarization is comparable to those of certain environmentally harmful perovskites, indicating that DIPAC has the potential to be a suitable alternative for high-temperature piezoelectric-based applications. The electrical conductivity of DIPAC was measured and the activation energy was determined to be 2.24 ± 0.03 eV. The system was found to be thermally activated, and this behavior can be attributed to the increase in cation thermal activation energy. This increase triggered the cation to jump to the next coordinating site. This jump induced a significant increase in the segmental vibrations energy, which in turn led to more segment motion to counter the increase in the hydrostatic pressure. Thermal agitations induced by the increase of the temperature enhanced the mobility of the free electrons significantly. Overall, the structural, optical, electronic, and electrical properties of DIPAC thin films measured and interpreted in this work indicate that these films could be potential candidates for the fabrication of a promising new generation of efficient multifunctional optoelectronic devices for a wide range of technological applications.

Author Contributions: Conceptualization, A.M.A., Q.M.A.-B. and A.T.; methodology, I.A.Q., I.A.A. and A.A.B.-S.; software, A.M.A., Q.M.A.-B. and A.T.; validation, A.A.A., B.A.A. and R.F.S.; formal analysis, Q.M.A.-B. and A.T.; investigation, A.M.A., Q.M.A.-B. and A.T.; resources, A.M.A., A.A.A. and R.F.S.; data curation, A.A.A. and R.F.S.; writing—original draft preparation, A.M.A., Q.M.A.-B., I.A.A., A.A.B.-S. and A.T.; writing—review and editing, I.A.Q., A.A.A., B.A.A. and R.F.S.; visualization, A.M.A., Q.M.A.-B. and A.T.; supervision, A.M.A. and R.F.S.; project administration, A.M.A. and R.F.S.; funding acquisition, A.M.A. and R.F.S. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The data that support the findings of this study are available from the corresponding author upon reasonable request.

Acknowledgments: We would like to acknowledge the financial support of the Scientific Research and Innovation Support Fund (Jordanian Ministry of Higher Education and Scientific Research), Project # 20210392. We would also like to acknowledge the continuing financial and logistic support provided by Khalifa University of Science and Technology, Abu Dhabi, United Arab Emirates. We would also like to acknowledge Jordan University of Science and Technology (JUST). Our thanks are extended to Mohammad-Ali H. Al-Akhras for helping our members use their films and biomedical laboratories.

Conflicts of Interest: The authors declare no conflict of interest.

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Article Threshold-Voltage Extraction Methods for Atomically Deposited Disordered ZnO Thin-Film Transistors

Minho Yoon

Department of Physics and Institute of Quantum Convergence Technology, Kangwon National University, Chuncheon 24341, Republic of Korea; minhoyoon78@gmail.com

Abstract: In this paper, we present a threshold-voltage extraction method for zinc oxide (ZnO) thin-film transistors (TFTs). Bottom-gate atomic-layer-deposited ZnO TFTs exhibit typical n-type enhancement-mode transfer characteristics but a gate-voltage-dependent, unreliable threshold voltage. We posit that this obscure threshold voltage is attributed to the localized trap states of ZnO TFTs, of which the field-effect mobility can be expressed as a gate-bias-dependent power law. Hence, we derived the current-voltage relationship by dividing the drain current with the transconductance to rule out the gate-bias-dependent factors and successfully extract the reliable threshold voltage. Furthermore, we investigated the temperature-dependent characteristics of the ZnO TFTs to validate that the observed threshold voltage was genuine. Notably, the required activation energies from the low-temperature measurements displayed an abrupt decrease at the threshold voltage, which was attributed to the conduction route change from diffusion to drift. Thus, we conclude that the reliable threshold voltage relationship with a low-temperature analysis.

Keywords: threshold voltage; localized trap states; ZnO; thin-film transistors

1. Introduction

Oxide semiconductors such as zinc oxide (ZnO), indium-gallium-zinc oxide (IGZO), and indium-zinc oxide (IZO) have been extensively investigated for their application in transparent electronics, the backplanes of large-area active-organic light-emitting-diode displays, and liquid crystal displays due to their high mobility, high transparency to visible light, and low processing temperatures [1–4]. However, oxide-semiconductor-based thin-film transistors (TFTs) suffer from severe threshold shifts during operation; therefore, compensation circuits are generally incorporated in their applications [5,6]. The threshold voltage (V_{th}) of TFTs is a gate voltage required to turn the devices on and is estimated using several methods, including a commonly used linear fitting method [7,8], a field-effect mobility derivation method [9], and a constant-current method [10]. However, the definition of the threshold voltage of TFTs is ambiguous. In the case of metal-oxide-semiconductor field-effect transistors (MOSFETs), the threshold voltage is defined as a gate voltage for the strong inversion point [11]. However, TFTs usually operate in an accumulation mode; hence, the threshold voltage of TFTs cannot be defined as in the case of MOSFETs. In some sense, the flatband voltage, a gate voltage for the zero-semiconductor band bending point, could be a more appropriate terminology for TFTs [12]. However, the threshold voltage of TFTs is used in the same way as that of MOSFETs. In addition, the near-threshold voltage operation of TFTs has received considerable attention for low-power applications [13]. Thus, the in-depth understanding of charge-transport behaviors' near-threshold voltage and the definition of the threshold voltage of TFTs are quite important. Indeed, due to localized states in the disordered oxide semiconductors, the charge-transport characteristics of TFTs are severely affected by interface and semiconductor trap states [14,15]. As a result, it is difficult to determine the conduction states and threshold voltage. Efforts

Citation: Yoon, M. Threshold-Voltage Extraction Methods for Atomically Deposited Disordered ZnO Thin-Film Transistors. *Materials* 2023, 16, 2940. https://doi.org/10.3390/ ma16082940

Academic Editors: Ricardo Lopez Anton, Jose Maria De Teresa and Sion Federico Olive Méndez

Received: 6 March 2023 Revised: 1 April 2023 Accepted: 5 April 2023 Published: 7 April 2023



Copyright: © 2023 by the author. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). to resolve these issues have led to several proposed approaches, such as the charge- and surface-potential-based compact models [16–18] and the semi-empirical model based on multi-frequent capacitance–voltage measurements [19]. These approaches generally yield promising results, but it seems that more reliable and practical methods are required to determine the threshold voltage for the disordered oxide semiconductor-based TFTs.

In this study, we explored the threshold-voltage extraction method and chargetransport behaviors near the threshold voltage of atomic-layer-deposited ZnO TFTs. Bottomgate, atomic-layer-deposited ZnO TFTs show typical n-type enhancement-mode transfer characteristics with a field-effect mobility of 3.1 cm²V⁻¹s⁻¹. However, defining the threshold voltage with the linear fitting method seems unreliable; as the gate bias increases, the threshold voltage changes. We posit that the localized states of ZnO TFTs are attributed to this ambiguous threshold voltage, of which the field-effect mobility is modeled as a power law [20–22]. In order to extract the reliable threshold voltage, we modified the current-voltage relationship by dividing the drain current with the transconductance. Following the modification, the gate-voltage-independent and reliable threshold voltage was successfully extracted. In addition, in order to ensure that the threshold voltage was genuine, we investigated the activation energies as a function of the gate voltage from the temperature-dependent transfer characteristics of the ZnO TFTs. The activation energy significantly decreased at the threshold voltage, which was attributed to the conduction route change from diffusion to drift. Therefore, we believe that the reliable threshold voltage of disordered ZnO TFTs can be determined by the proposed method.

2. Materials and Methods

Bottom-gate top-contact (BGTC) ZnO TFTs were fabricated as shown in the optical microscope image in Figure 1a. A 200 nm thick p⁺-Si/SiO₂ wafer coated with a 10 nm thick Al₂O₃ was used as the substrate, and a 6 nm thick ZnO film was deposited by cyclic atomic layer deposition (ALD) at 80 °C using diethylzinc (DEZ, Aldrich, St. Louis, MO, USA) and water as zinc and oxygen precursors, respectively. After patterning the ZnO layer by a conventional lift-off process, 50 nm thick Al source and drain electrodes were deposited by thermal evaporation and patterned using a shadow mask, which had a width and length of 1000 and 360 µm, respectively. To extract the intrinsic conductance of the ZnO channel, a four-point probe source and drain configuration was used, of which the voltage-probing electrodes (V_1 and V_2) were placed at 120 and 240 μ m in the channel. The geometric capacitance of the dielectric was measured to be 16.4 nF cm⁻² at 1 kHz, using an LCR meter (HP4284A, Agilent Technologies, Santa Clara, CA, USA). The thickness of the films was measured with an ellipsometer (AutoEL-II, Rudolph Research, Hackettstown, NJ, USA) and confirmed with an atomic force microscope (XE100, Park Systems, Suwon, Korea). A magnetic-sector-based instrument (TOF.SIMS-5, ION-TOF) was used for time-of-flight secondary ion mass (SIMS) analysis, with a Bi+-ion beam (30 keV) as the primary ion source to detect negative secondary ions. For the depth profiling, the etching source of Cs^+ (1 keV) was used and the analysis area was $100 \times 100 \ \mu m^2$. The homemade Hall measurement system was used for analyzing the ZnO films; the electromagnet (up to 1 T) was placed beneath the probing stage, and the electrical signals were recorded with a semiconductor parameter analyzer (Model HP4155C, Agilent Technologies). The current-voltage (I-V) characteristics of the transistors were also investigated with the semiconductor parameter analyzer (Model HP4155C, Agilent Technologies). A liquid-nitrogen cooling cryostat was used for temperature-variable current-voltage measurements. The temperature range was from 180 to 300 K. The extrinsic field-effect mobility of the TFTs in a linear regime was estimated by the following equation:

$$\mu_{lin} = \frac{1}{C_i V_{ds}} \frac{L}{W} \frac{\partial I_{ds}}{\partial V_{gs}} \tag{1}$$

where I_{ds} is the drain current, V_{gs} is the gate voltage, C_i is the geometric dielectric capacitance, V_{ds} is the drain voltage, and L and W are the channel length and width, respectively.



Figure 1. (a) Optical microscopy image of the ZnO TFTs with a four-point probe configuration. (b) Transfer characteristics (I_{ds} vs. V_{gs}) of the ZnO TFTs. (c) The threshold-voltage extraction of the ZnO TFTs with the gate bias range up to 40 (red), 60 (blue), and 80 (black) V, respectively. (d) Output characteristics (I_{ds} vs. V_{ds}) of the ZnO TFTs.

3. Results

Figure 1b displays the typical n-type transfer characteristics (I_{ds} vs. V_{gs} at V_{ds} = 1 V) of the ZnO TFTs [23]. As the gate bias increased, the electron current (I_{ds}) increased from $\sim 10^{-11}$ to $\sim 10^{-6}$ A, and the field-effect mobility from the transconductance also gradually increased, reaching a maximum of 3.1 cm²V⁻¹s⁻¹ at V_{gs} = 80 V. However, the threshold voltage (V_{th}) of ZnO TFTs was difficult to determine. As shown in Figure 1c, using the widely used linear fitting method, the threshold voltage can be estimated to be 25 V when extracted up to the gate bias of 40 V, but it increased to 36 and 42 V when extracted up to the gate bias of 60 and 80 V, respectively. The threshold voltage of TFTs is a widely used key parameter for investigating the interface trap states and the stability of the devices [24,25]. Thus, if the threshold voltage is not reliable, as in ZnO TFTs, the analysis of the devices leads to misinterpreted consequences. The current-voltage characteristics of ZnO TFTs with a two-terminal geometry are the sum of the channel resistance (R_{ch}) and the contact resistance (R_c). If the contact resistance (R_c) is not negligible, the threshold voltage may be ambiguous, as in ZnO TFTs, because the contact resistance decreases with the increasing gate voltage [26,27]. To address this issue, as schematically illustrated in Figure S1a, the contact-effect-removed current-voltage characteristics of the ZnO TFTs were investigated by measuring the potential distribution in the channel; then, the intrinsic threshold voltage was revisited. However, the obscure threshold voltage can still be seen in Figure S1b, which was 25, 37, and 46 V for the gate biases of 40, 60, and 80 V, respectively. Figure 1d shows the corresponding output characteristics (I_{ds} vs. V_{ds}) of the ZnO TFTs, which revealed an ohmic contact behavior.

As reported elsewhere, charges in amorphous or polycrystalline disordered semiconductors move through localized states via thermally activated hopping [28–30]. Thus, as the gate bias increases, the localized states are occupied by the induced charges, resulting in increased field-effect mobility, modeled as the power law $\mu = \mu_0 (V_{gs} - V_{th})^{\alpha}$, where α is the power law exponent. As a result, the drain current (I_{ds}) can be expressed as the gatebias-dependent power law $I_{ds} = \mu_0 C_i WL^{-1} (V_{gs} - V_{th})^{\alpha+1} V_{ds}$. Thus, the widely used linear fitting method results in the arbitrary extraction of ZnO TFTs because the drain current (I_{ds}) is not linearly dependent on the gate bias. Hence, we attempted to modify the thresholdvoltage extraction method based on the power-law-dependent relations. By expressing the drain current (I_{ds}) and transconductance (g_m) of the TFTs as gate-bias-dependent power law equations, a power-law term-removed current relation can be derived by dividing the drain current with the transconductance, as in the following equation. Using this relation, the exponent of α and the threshold voltage can be estimated.

$$I_{ds} = \mu_0 C_i \frac{W}{L} (V_{gs} - V_{th})^{\alpha + 1} V_d$$
⁽²⁾

$$g_m = \frac{\partial I_{ds}}{\partial V_g} = (\alpha + 1)\mu_0 C_i \frac{W}{L} (V_{gs} - V_{th})^{\alpha} V_d \tag{3}$$

$$\frac{I_{ds}}{g_m} = \frac{\left(V_{gs} - V_{th}\right)}{\left(\alpha + 1\right)} \tag{4}$$

Figure 2a shows the extraction plot of I_{ds}/g_m for the ZnO-based TFTs. From the linear fitting of the plot, the exponent of α and the threshold voltage were estimated to be 0.92 and 15 V, respectively. In addition, as in Figure 2b, the current–voltage characteristics of the ZnO TFTs were retraced using the power-law-term-corrected relation $I_d^{1/(\alpha+1)} = (\mu_0 C_i WL^{-1}V_{ds})^{1/(\alpha+1)}$ ($V_{gs} - V_{th}$), and the threshold voltage was re-extracted. Surprisingly, the power-law-term-corrected transfer curve changed to a relatively linear curve, enabling us to extract the threshold voltage with the gate-bias-independent value of 15 V. In addition, the value was consistent with the value from the modified extraction plot of I_{ds}/g_m . Thus, we regard the extracted threshold voltages as reliable. However, it is still unconfirmed whether the threshold voltage is genuine. As aforementioned, the conduction states in disordered semiconductor-based TFTs are generally difficult to determine. Hence, to validate that the extracted threshold voltage is authentic, we investigated and carefully analyzed the temperature-dependent current–voltage characteristics of the ZnO TFTs from 180 to 300 K.



Figure 2. (a) The modified plot of I_d/g_m for the ZnO TFTs. (b) The power-law-term-removed threshold-voltage extraction of the ZnO TFTs.

Figure 3a depicts the temperature-dependent transfer characteristics of the ZnO TFTs. Fundamentally, charge carriers in transistors (including MOSFETs and TFTs) are thought to be mainly transported by the diffusion of carriers below the threshold voltage and by the drift of carriers above the threshold voltage [11,17,31]. If one can decouple the diffusion current from the total drain current, the threshold voltage of the TFTs can be determined [32]. However, direct decoupling in disordered semiconductor-based TFTs is hardly conducted because both diffusion and drift currents occur through thermally activated transports. To this end, we conceived that if the activation energies for conduction were extracted and compared, the threshold voltage of the TFTs could be determined. The required activation energies for diffusion and drift are different. Hence, using the Meyer–Neldel rule of $I(V_{qs}) = I_0 exp(-E_a/k_{BT})$, we investigated the activation energies (E_a) as in Figure 3b [28,29]. Figure 3c displays extracted activation energies (E_a) as a function of the gate voltage. Notably, at the low-gate-voltage regime ($V_{gs} < 15$ V), the activation energy (Ea) was deduced to be as high as 110 meV, but it sharply decreased at the gate voltage of 15 V and gradually decreased to ~40 meV (V_{gs} > 40 V). Although a detailed study on activation energies for diffusion and drift currents in ZnO films is not provided in this study, this abrupt decrease in activation energy at the threshold voltage is attributed to the conduction route change from diffusion to drift. The diffusion current, which is the charge transport driven by the concentration gradient, requires a higher activation energy than the drift current, which is driven by electrical potential. In addition, the deduced voltage of 15 V was consistent with the value from the modified extraction plot. Furthermore, the conduction route change was reconfirmed by investigating the localized (trap) density of states (DOS), g(E), of the ZnO TFTs. Assuming the gate-dependent activation energy is closely related to the energetic difference between the Fermi level and conductive states, the areal density of states of the ZnO TFTs is extracted using following equation [29,30]:

$$g(E) = \frac{C_i}{q} \left(\frac{dE_a}{dV_{gs}}\right)^{-1}$$
(5)

where E_a is the gate-dependent activation energy from the Meyer–Neldel rule $I(V_{gs}) = I_0 \exp(-E_a/k_{BT})$. As illustrated in Figure 3d, at the low-gate-bias regime ($V_{gs} < 15$ V), as the gate bias increased, the trap density was estimated to be as low as $\sim 10^{12}$ states $eV^{-1}cm^2$, but it increased rapidly to $\sim 10^{13}$ states $eV^{-1}cm^2$. However, at the high-gate-bias regime ($V_{gs} > 15$ V), it was estimated to be as high as $\sim 10^{14}$ states $eV^{-1}cm^2$, but it slowly increased. Although trap states are literally trap states, the trap states in ZnO films can act as conduction states in the forbidden gap. Thus, the conduction occurs as follows: below the threshold voltage, the density of the mobile charges that involve the conduction rapidly increases, causing the conduction by vertical state-to-state hopping. In contrast, above the threshold voltage, the density of the mobile charges is saturated; thus, horizontal state-to-state hopping leads to the conduction. This vertical to horizontal hopping change occurs due to the conduction route change, from concentration-limited current (diffusion) to electric-field-driven current (drift). In addition, the deduced voltage of the ZnO TFTs from the low-temperature analysis, 15 V, was consistent with the voltage from the modified extraction plot of I_{ds}/g_m . Thus, we can conclude that the threshold voltage acquired by the proposed method is reliable and genuine.



Figure 3. (a) Temperature dependence of the transfer curves of the ZnO TFTs. (b) Plots of $Ln(I_D)$ as a function of 1/T of the ZnO TFTs. (c) Extracted activation energies as a function of gate voltage. Inset: Extracted activation energies for the gate voltage up to 80 V. (d) Extracted charge trap density of states (DOS) of the ZnO TFTs.

To further ensure that the threshold-voltage extraction method is applicable for threshold-voltage-shifted ZnO TFTs, we fabricated Al₂O₃-coated ZnO TFTs. Figure 4a shows the transfer characteristics (I_{ds} vs. V_{gs} at V_{ds} = 1 V) of the Al₂O₃-coated ZnO TFTs, clearly displaying the threshold voltage shifts. As reported elsewhere, the top Al₂O₃ layer on the ZnO films causes conductive changes in the films and leads to significant threshold voltage shifts in the TFTs [23]. Aluminum and hydrogen can offer additional electrons in ZnO films [33]. The cyclic atomic deposition process for the top Al_2O_3 layer is conducted at 110 °C for hours; hence, the ions can diffuse into the ZnO side, leading to electron doping. The time-of-flight secondary ion mass (SIMS) analysis in Figure 4b shows that aluminum (Al-) and hydrogen (H-) ions significantly diffused into the films. In addition, Hall measurements of the films in Figure 4c display that conductive ZnO films were formed by the Al₂O₃ deposition. As the thickness of the top Al₂O₃ layer increased, the carrier concentration rose from ~10¹⁵ to ~10¹⁹ cm⁻³ and the resistivity decreased from ~10⁴ to ~10⁻¹ ohm-cm. As seen in Figure 4d, using the modified extraction method of $I_{ds/gm}$, the threshold voltages for 1 and 3 nm thick Al_2O_3 -coated ZnO TFTs were successfully determined by 9 and -53 V, respectively. Moreover, when investigating the temperature-dependent transfer characteristics of the Al_2O_3 -coated ZnO TFTs in Figure 4e, the activation energies (E_a) of the 1 and 3 nm thick Al_2O_3 -coated ZnO TFTs in Figure 4f showed abrupt decreases at 9 and -53 V, respectively. In addition, the power law exponent revealed the degree of the localization of the conduction states. The exponent of pure ZnO TFTs was estimated to be 0.92, whereas they were 0.87 and 0.85 for the 1 and 3 nm thick A₂O₃-coated ZnO TFTs, respectively.

A

Notably, the field-effect mobility of pure ZnO TFTs was 3.1 cm²V⁻¹s⁻¹, but it increased to 3.9 and 7.1 cm²V⁻¹s⁻¹ for the 1 and 3 nm thick Al₂O₃-coated ZnO TFTs, respectively. This increase in mobility as the exponent decreases is attributed to the conduction states of the charge transport. When the conduction takes place in deep localized states, the charge transport is strongly dependent on the gate bias, resulting in a high power-law exponent. However, when in shallow localized states (due to doping), the charge transport is less affected by the gate bias, leading to a low power-law exponent. The device parameters are listed in Table 1.



Figure 4. (a) The transfer curves of the Al₂O₃-coated ZnO TFTs. (b) The SIMS depth profiling of the Al₂O₃-coated ZnO film. (c) Conductivity and carrier concentrations of the ZnO films with the top Al₂O₃ layer. (d) The modified I_{ds}/gm plot for the Al₂O₃-coated ZnO TFTs. (e) Temperature dependence of the transfer curves of the Al2O3-coated ZnO TFTs. (f) Extracted activation energies as a function of gate voltage for the Al2O3-coated ZnO TFTs.

		Power-Law V _{turn-on} (N Exponent			V_{th} (V)	
	μ (cm ² V ⁻¹ s ⁻¹)		V _{turn-on} (V)	Linear Fitting (V _{gs})	I_{ds}/g_m	E_a Analysis
ZnO	3.1	0.92	8	25/36/42 (40/60/80)	15	15
1 nm thin Al ₂ O ₃ -coated ZnO	3.9	0.87	-5	21/28/41 (40/60/80)	9	9
3 nm thin Al ₂ O ₃ -coated ZnO	7.1	0.85	-72	-42/-26/-18 (-20/20/80)	-53	-53

Table 1. Summary of the device parameters for the ZnO and Al₂O₃-coated ZnO TFTs.

Moreover, to verify that the method is applicable for amorphous semiconductors, TFTs based on a well-known amorphous semiconductor, indium-gallium-zinc oxide (IGZO), were fabricated and their threshold voltage was investigated. The bottom-gate top-contact sputter-deposited IGZO TFTs on a chemically cleaned 200 nm thick p^+ -Si/SiO₂ wafer displayed typical n-type transfer characteristics (I_{ds} vs. V_{gs} at $V_{ds} = 1$ V), as seen in Figure S2a; the extrinsic field-effect mobility from the transconductance increased, reaching 15.2 cm²V⁻¹s⁻¹ at $V_{gs} = 40$ V. As seen in Figure S2b, the threshold voltage (V_{th}) of the IGZO TFTs also varied with the gate bias, which was estimated to be 17, 22, and 27 V for the gate biases of 25, 30, and 40 V, respectively. However, these arbitrary threshold voltages changed to the definitive value of 14 V after applying the modified extraction method, I_{ds}/g_m , as in Figure S2c. In addition, the power-law-term-corrected current relation of the IGZO TFTs also showed a distinctive linear curve in Figure S2d, and the threshold voltage was again deduced to be 14 V. It was also consistent with the value from the modified extraction plot of I_{ds}/g_m . As a result, we can state that the threshold voltages of disordered oxide transistors can be easily determined from the transfer curve at room temperature using the proposed threshold-voltage extraction method of I_{ds}/g_m .

4. Discussion

Based on the experiments and findings, we can now understand the operation of the accumulation-mode ZnO TFTs, in which threshold and flatband voltages can be determined due to the deep and shallow trap states. As seen in Figure 5a,b, below the flatband voltage, which is estimated with the turn-on voltage [32], charges cannot be transported, because the induced charges are mainly assigned to fill the deep trap states. However, as the gate bias increases above the flatband voltage, deep trap states are filled with gate-induced charges, and the charges can be transported. However, the charges are transported through the deep trap states, mainly transported by concentration-gradient-driven currents (diffusion current). Diffusion currents occur due to the inverted charges in the depletion region of MOSFETs and due to accumulated charges in the deep trap states of TFTs. When the gate voltage further increases above the threshold voltage, the deep trap states are almost filled with the charges, enabling electric-field-driven currents to transport the charges through the shallow trap states (drift current). Capacitance-voltage (C-V) measurements could be used to characterize the interfacial defects of TFTs [14]. However, in this case, the deposition of aluminum electrodes on ultra-thin atomically deposited ZnO films for a metal-oxide-semiconductor structure causes electron doping [33] and alters the threshold voltage of the disordered TFTs. For this reason, we attempted to detect the trap states of the ZnO TFTs using the TFTs' structure, by measuring their low-temperature characteristics. Additionally, proving that the method is applicable more generally would require thresholdvoltage extraction using other semiconductors, such as p-type or ambipolar semiconductors. Nevertheless, based on the results, we believe that the proposed method is reliable and applicable to determine the threshold voltages of disordered oxide semiconductor TFTs.



Figure 5. (a) The transfer curves and the power-law-term-removed threshold-voltage extraction of the ZnO TFTs. (b) Extracted charge trap density of states (DOS) of the ZnO TFTs.

5. Conclusions

In this study, the threshold-voltage extraction methods of bottom-gate atomic-deposited ZnO TFTs were investigated. The ZnO TFTs display typical n-type enhancement-mode transfer characteristics, but the threshold voltage is difficult to determine. By considering that the obscure threshold voltage is attributed to the localized states, we derived current-voltage relations decoupled with the gate-bias-dependent factor and successfully extracted the reliable threshold voltage. Furthermore, to ensure the threshold voltage was genuine, the temperature-dependent current-voltage characteristics of the ZnO TFTs were investigated. Using the Meyer-Neldel rule, the activation energy as a function of the gate voltage was deduced. Notably, the activation energy significantly changed at the threshold voltage, which is attributed to the conduction route change from diffusion to drift. The diffusion current below the threshold voltage required higher energy than the drift current. More dramatically, the change in density of the ZnO TFTs states also revealed the conduction route change. The trap density increased rapidly from 10¹² to 10¹³ states $eV^{-1}cm^2$ below the threshold voltage, whereas it saturated to 10^{14} states $eV^{-1}cm^2$ above the threshold voltage. This significant change in trap density implies that the increment in the mobile charges released from the deep trap state led to conduction at the low-voltage regime (diffusion), while the electric-field-affected mobile charges resulted in conduction at the high-gate-bias regime (drift). We thus conclude that our proposed method offers practical and theoretical benefits for extracting the threshold voltage and understanding the operation of disordered accumulation-mode ZnO TFTs.

Supplementary Materials: The following supporting information can be downloaded at: https: //www.mdpi.com/article/10.3390/ma16082940/s1, Figure S1: Device parameter analyses of ZnO TFTs with a four-point probe configuration; Figure S2: Device parameter analyses of IGZO TFTs.

Funding: The authors acknowledge the financial support from the Basic Science Research Program (Sejong Fellowship) through the National Research Foundation of Korea (NRF), funded by the Ministry of Education (NRF-2022R1C1C2008865).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Conflicts of Interest: The author declares no conflict of interest.

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Article



Investigation of TiO₂ Deposit on SiO₂ Films: Synthesis, Characterization, and Efficiency for the Photocatalytic Discoloration of Methylene Blue in Aqueous Solution

Yuliana de Jesús Acosta-Silva ^{1,*}, Manuel Toledano-Ayala ¹, Salvador Gallardo-Hernández ², Luis A. Godínez ³ and Arturo Méndez-López ^{1,*}

- Research and Postgraduate Division, Faculty of Engineering, Autonomous University of Queretaro (UAQ), University Center, Querétaro 76010, Mexico
- ² Department of Physics, Center for Research and Advanced Studies of the National Polytechnic Institute, México City 07360, Mexico
- ³ Centro de Investigación en Química para la Economía Circular, CIQEC, Faculty of Chemistry, Autonomous University of Queretaro, University Center, Querétaro 76010, Mexico
- * Correspondence: yuliana.dejesus.acosta@uaq.mx (Y.d.J.A.-S.); arturo.mendez@uaq.mx (A.M.-L.)

Abstract: TiO₂-SiO₂ thin films were created on Corning glass substrates using a simple method. Nine layers of SiO₂ were deposited; later, several layers of TiO₂ were deposited, and their influence was studied. Raman spectroscopy, high resolution transmission electron spectroscopy (HRTEM), an X-ray diffractometer (XRD), ultraviolet-visible spectroscopy (UV-Vis), a scanning electron microscope (SEM), and atomic force microscopy (AFM) were used to describe the sample's shape, size, composition, and optical characteristics. Photocatalysis was realized through an experiment involving the deterioration of methylene blue (MB) solution exposed to UV-Vis radiation. With the increase of TiO₂ layers, the photocatalytic activity (PA) of the thin films showed an increasing trend, and the maximum degradation efficiency of MB by TiO₂-SiO₂ was 98%, which was significantly higher than that obtained by SiO₂ thin films. It was found that an anatase structure was formed at a calcination temperature of 550 °C; phases of brookite or rutile were not observed. Each nanoparticle's size was 13–18 nm. Due to photo-excitation occurring in both the SiO₂ and the TiO₂, deep UV light (λ = 232 nm) had to be used as a light source to increase photocatalytic activity.

Keywords: dip-coating; TiO₂-SiO₂ thin films; photocatalytic processes; methylene blue; sol-gel; UV-visible light

1. Introduction

Diverse colors and other organic and inorganic contaminants are found in textile industry wastewater. Twelve percent of synthetic textile dyes, including eriochorome black-T (EBT), methyl orange (MO), rhodamine B, and methylene blue (MB), are thought to be lost during the dyeing process, and approximately 20% of these dyes are carried as waste to industrial wastewater treatment facilities [1]. Among these chemicals, MB is one of the most popular, as it is used not only as a dye for wool, hair coloring compounds, paper prints, and cotton, but also as an antiseptic, among other health-related purposes [2]. MB, on the other hand, is regarded as biologically dangerous, because it is a powerful carcinogen for marine animals, and in humans severely irritates the eyes, causes convulsions, irritates sensitive skin, and induces tachycardia [3]. MB also reacts with various substances, which makes the treatment of aqueous effluents containing MB a difficult task [4]. On the other hand, advanced oxidation processes (AOPs) are regarded as efficient approaches for the elimination of organic contaminants from aqueous solutions, such as MB. These procedures are based on the fact that hydroxyl radicals (HO•), which have a particularly high oxidation potential, rapidly oxidize the majority of organic contaminants

Citation: Acosta-Silva, Y.d.J.; Toledano-Ayala, M.; Gallardo-Hernández, S.; Godínez, L.A.; Méndez-López, A. Investigation of TiO₂ Deposit on SiO₂ Films: Synthesis, Characterization, and Efficiency for the Photocatalytic Discoloration of Methylene Blue in Aqueous Solution. *Nanomaterials* 2023, *13*, 1403. https://doi.org/ 10.3390/nano13081403

Academic Editors: Ricardo Lopez Anton, Jose Maria De Teresa and Sion Federico Olive Méndez

Received: 13 March 2023 Revised: 5 April 2023 Accepted: 11 April 2023 Published: 19 April 2023



Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). with great efficiency (generally in the range 108–1011 $M^{-1} s^{-1}$) [5–7]. One way to produce OH radicals is by the oxidation of surface adsorbed H_2O molecules, using photo-excited semiconductor materials [8]. Titanium dioxide (TiO2) is an excellent photocatalyst, due to its low cost, nontoxicity, and good chemical and mechanical stability [9,10]. Therefore, TiO₂ is used in solar cells [11], self-cleaning glasses [12], antifogging windows [13], and as a photocatalytic material for the degradation of contaminants in wastewater [14]. The ability of illuminated TiO_2 to produce OH radicals depends on specific features of TiO_2 , such as the size of the semiconductor crystallites and their surface area [15]. The photo-physical and chemical properties of the TiO₂ material allows for coupling to other semiconductors; in this regard, SiO_2 is a practical option because of its great mechanical strength and good thermal stability [16]. Amorphous SiO₂ has also been demonstrated to have a high surface area and outstanding adsorption capacity, making it an effective substrate for semiconductor films [17]. Zhou et al., for example, demonstrated that mixed metal oxides (TiO₂-SiO₂) improve the photocatalytic efficiency of the individual materials, because it enhances the materials' adsorption properties and increases their concentration of surface hydroxyl groups in the thin film. In addition, SiO₂ was shown to promote a large surface area and an appropriately porous structure [15]. There are abundant reports in the literature focusing on the synthesis and characterization of TiO₂-based photocatalysts; in this context, we believe that in addition to phase structure, doping, and composite design and synthesis, the study of TiO₂ layers grown by the sol-gel dip-coating method on top of the SiO_2 semiconductor material films could be useful for the development of novel and efficient photocatalytic surfaces. This communication, therefore, presents the structural, morphological, and optical properties of the SiO_2/TiO_2 composite films proposed, as well as an exploration of their photocatalytic performance.

2. Experimental Details

2.1. SiO₂ Thin Films

SiO₂ solutions were prepared by dissolving a certain amount of triblock copolymer (BASF, EO106-PO70-EO106, F127) in ethanol (J.T. Baker, Querétaro, Mexico), with constant stirring for 1 h at 37 °C. Then, 0.7 mL of HCl (J.T. Baker) were added by drops, and the solution was continuously stirred for 30 min. After adding 5.5 mL of TEOS to the mixture, it was agitated for 24 h at 36 °C. The resulting transparent and homogeneous phase was then employed to prepare thin films on glass substrates (Corning 2947, area $2.5 \times 7.5 \text{ cm}^2$) using the dip-coating technique. Figure 1a shows a scheme describing the dip-coating process employed in this work. The previously cleaned substrate is dipped into a solution of the precursors (the material to be deposited) and then withdrawn vertically at a controlled speed. For this purpose, the homemade system shown in Figure 1b (operating at a withdrawal rate of 8 cm/min) was utilized to obtain SiO₂ thin films containing nine sequential coatings; each layer was prepared by drying the coating at 250 °C (calcination temperature) over two hours at a rate of 2 °C/min ramp.

2.2. TiO₂-SiO₂ Thin Films

Thin films were prepared by immersion as reported in a previous section, in a solution containing titanium (IV) isopropoxide (Sigma-Aldrich Co., Querétaro, Mexico), 2-propanol (J.T. Baker), and hydrochloric acid (37% HCl). The TiO₂ thin films were deposited using the 2 cm/min removal rate for the dip coating process, and in this case, the films surveyed consisted of coatings of 5, 7, and 9 layers. As was indicated for the SiO₂ films, each layer was dried at 250 °C for 3 min, and once each film was completed with the corresponding number of layers, the surface modified material was calcined at 550 °C for 1 h. In terms of the cross-sectional characterization of the composite films under study, we carried out thickness measurements using a KLA TENCO P-15 profilometer as described in the experimental section. In this way, while the thickness of the SiO₂ films under study corresponded to



~250 nm, the thicknesses of the TiO_2 material films consisted of ~171, 219, and 262 nm, depending on the number of deposited TiO_2 layers (5, 7 and 9, respectively).

Figure 1. (a) Sequential steps of the sol–gel dip-coating method for thin film deposition. (b) Dip coating system assembled in the NanoBiotechnology and Photocatalysis Laboratory—UAQ. This system is used for the production of various thin films.

2.3. Structural, Optical, and Morphological Characterization of the Films

UV-Vis measurements were carried out using an Evolution 220 UV-Vis Spectrophotometer. X-ray diffraction experiments were carried out using a Philips X-ray diffractometer (PANalytical's X'pert PRO X-ray diffractometer, Malvern, UK) that employs a Cu-K α radiation with a of 0.15405 nm in the $20 \le 2\theta \le 80^\circ$ range. The voltage and current settings were 30 kV and 40 mA, respectively. The samples were continuously scanned with a step size of 0.02° (20) and a count time of 1 s per step. Structural properties were also studied using Raman spectroscopy that collected data using a Labram-Dilor Raman spectrometer equipped with a He-Ne laser exciting source, operating between the wavelengths of 200 and 800 nm at ambient temperature (AT). The roughness and surface topography were examined by AFM (Park Scientific Inst. System, Suwon, South Korea). Using a scanning electron microscope (SEM, JEOL JSM-6300, Tokyo, Japan), surface pictures were acquired. Prior to the acquisition of images by high-resolution transmission electron microscopy, tiny bits of films were scraped. JEOL JEM 2010 microscope with an acceleration voltage of 200 kV was used for this objective. Typically, the magnification ranged from \times 400,000 to \times 500,000. At the camera length L = 20 cm, selected area electron diffraction (SAED) was carried out. Thickness measurements were made using a KLA TENCOR P-15 profilometer (Milpitas, CA, USA).

2.4. Photocatalytic Activity Evaluation

The PA of films was determined at AT by assessing the MB discoloration kinetics of aqueous solutions of 5.4 mg/L (1.88×10^{-5} mol/L) under UV radiation. In this way, 3 mL of the aqueous MB solution were poured into a standard quartz cell, and later, a TiO₂-SiO₂ coated substrate was placed vertically inside the cell (with a 2 cm² exposed area). Five quartz cells prepared in this way were used for each thin film under study. The 15 W

lamp used to produce the irradiation light had a 254 nm wavelength (G15T8 germicidal lamp as the exciting source). Five centimeters separated the quartz cells from the lamp. A Thermo ScientificTM Evolution 220 Spectrophotometer was used to measure the optical absorbance of the test solution every 60 min for the course of the 5 h of total irradiation. The absorbance peak reduction for MB was examined in the range of 400 to 800 nm. The residual methylene blue concentration was calculated using the absorbance data at 664 nm employing the Beer-Lambert's law.

3. Results and Discussion

3.1. X-ray Diffraction

The XRD patterns of the thin films of TiO_2 deposited on mesoporous SiO_2 thin films are shown in Figure 2. The JCPDS-ICDD powder diffraction database was used to identify the crystal phases and matching miller indices. The JCPDF number for TiO_2 is 00-21-1272. The anatase phase of TiO_2 predominated in all the samples' patterns; no other phase was present. The samples diffraction peaks were seen at 20 values of 25.3°, 37.8°, 38.6°, 48.1°, 53.9° , 55.1° , 62.7° , 68.9° , 70.4° , and 75.1° and could be perfectly correlated with the (101), (004), (112), (200), (105), (211), (204), (116), (220), and (215) crystal planes of anatase TiO₂. All peaks were well indexed according to the standard patterns. The increase in the number of TiO₂ coatings resulted in thin films that exhibited higher intensities, indicating an increase in crystallinity owing to the higher presence of TiO_2 layers on top of SiO_2 . No phase transformation occurred for any of the samples. Moreover, all samples displayed a preferential orientation growth at (101) the plane (see Figure 2), which can be attributed to the plane's low surface energy value [18]. According to Zhang et al. [19], the phase transformation of TiO₂ only takes place at temperatures above 900 °C. An estimation of average crystallite size was calculated using the Scherrer equation; 5TiO₂-9SiO₂, 7TiO₂-9SiO₂, and 9TiO₂-9SiO₂ samples correspond to 13, 14, and 18 nm, respectively. For these calculations, Equation (1) was used as follows [20]:



$$d = \frac{K\lambda}{\beta\cos\theta} \tag{1}$$

Figure 2. X-ray diffraction patterns for samples of TiO_2 over SiO_2 annealed. The tetragonal phase is linked to thin films of TiO_2 that correspond to the (hkl) indices.

 λ the wavelength of the radiation (1.54056 for CuK radiation), θ is Bragg's angle, β the full width at half maximum (FWHM) intensity in radians, d the average thickness of the crystal in a direction normal to the diffracting plane (hkl), and *K* is Scherrer constant.

Equations (2) and (3), respectively, express two additional structural parameters known as the dislocation density (δ) and the microstrain (ε) [21]:

6

ε

$$\delta = \frac{1}{d^2} \tag{2}$$

$$=\frac{\beta}{4\tan\theta}\tag{3}$$

Figure 3 illustrates how the number of layers of TiO_2 affected the variance in dislocation density, crystallite size, and strain in the thin films studied. The following values demonstrate that the strain decreases as the number of layers are enhanced and the crystallite size increases. The same trend of the crystallite size was also reported by Lin et al. [22] for ZnO films made with various thicknesses. The relationship between the two variables can be explained by the collective fusing of small crystallite particles into larger ones, which leads to decreased densities of nucleation centers and, in turn, internal strain [23,24].



Figure 3. Crystallite size and strain of TiO₂-SiO₂ thin films based on the quantity of dip-coating layers.

3.2. UV-Vis

Based on the UV-vis characterization experiments, transmittance (T), and reflectance (R) data on the TiO₂-SiO₂ thin films were obtained in the 300–1100 nm wavelength window. Figure 4a–c shows that transmittance spectra are characterized by maxima and minima values of different orders. As the film thickness increases (to 5, 7, and 9 layers), the location of a particular transmittance extrema (maxima) shifts towards longer wavelengths. Similar results have been reported for five TiO₂ layers on SiO₂ [25]. Also, the thin films under investigation displayed a dramatic decline in transmittance in the ultraviolet spectrum. It was found that the absorption edge of the transmittance moves towards red in the ultraviolet region as the film thickness grows for TiO₂ thin films produced with the same withdrawal speed. Figure 4d shows the optical reflectance as a function of wavelength (λ). When there is an increase in the number of layers, the reflectance rises, which is more significant within the visible region. The band gap between conduction (CB) and valence bands (VB), a crucial optical characteristic of thin films, is calculated using the well-known Tauc equation, as given in Equation (4) [26]:

$$\alpha h\nu = A \left(h\nu - E_g \right)^n \tag{4}$$



Figure 4. Determination of *E*_g energy for TiO₂-SiO₂ thin films. (**a**–**c**) Spectral dependence of T(λ) and R(λ) coefficients, (**d**) UV–Visible reflectance spectra of TiO₂-SiO₂ thin films, (**e**) *E*_g determined by optical method using $(\alpha h\nu)^{1/2}$ vs. hν plots of thin films deposited with different numbers of TiO₂-SiO₂ layers.

Here, the constant *A* is related to the effective masses (electrons and holes), the input photon energy is represented by $h\nu$, the optical bandgap is represented by E_g , and the exponent n is dependent on the kind of travnsition. When n = 2 denotes permitted indirect transitions, 3 denotes forbidden indirect transitions, 1/2 denotes permissible direct transitions and 3/2 for forbidden direct transitions. When the line is intercepted at the energy axis ($\alpha = 0$) yields the band gap (Figure 4e). Here, it can be shown that the E_g values decrease as the number of TiO₂ layers increases. The E_g value for 9TiO₂-9SiO₂ was found to be 3.34 eV, as shown in Figure 4e, which is comparable to observations reported by other groups [27–29]. The bandgap energy in Figure 4e for 5TiO₂ is 3.53 eV, and in this regard, it has been reported that for powders light absorption (as well as the bandgap of TiO₂), does

not change when several layers of TiO_2 are present. For interacting semiconductor layers, however, it is common to observe a decrease in the band gap due to an increase in the grain size of TiO_2 layers [30]. Also, some sub-bands form due to defect levels in the forbidden band of TiO_2 , thereby reducing the "band-gap energy" [31].

3.3. Raman Spectroscopy

Raman measurements of the layers of TiO₂ deposited on mesoporous SiO₂ were investigated as described in the experimental section. The resulting Raman data in the 190–800 cm⁻¹ range (Figure 5) show that the anatase titania vibrational modes E_g , B1g, A1g+B1g, and E_g have been assigned to peaks at 197, 394, 516, and 637 cm⁻¹ in all samples, respectively [32,33]. While the peaks located at 197 and 637 cm⁻¹ agree with the E_g mode (attributed to the symmetric stretching vibration of O-Ti-O) and a B_{1g} mode corresponds to the peak at 394 cm⁻¹ (which is due to the symmetric bending vibration of O-Ti-O), the A_{1g} mode arises from the asymmetric bending vibration of this same bond. The latter mode also overlaps with the remaining B_{1g} mode, producing the emission of a signal with a peak at 516 cm⁻¹. This mode was extensively investigated by Otakar et al. [33]. The intensity of the peaks is normally affected by the number of layers [34]. The Raman spectra obtained indicate that the surface of the TiO₂ thin films is characterized by a pure anatase phase without the production of impurity phases, because there are no rutile (447 and 612 cm⁻¹) [35] or brookite (246 and 449 cm⁻¹) [36] phase peaks present. As was previously discussed, these results are consistent with XRD data.



Figure 5. Raman spectrum of TiO₂-SiO₂ thin films heated to 550 °C in air (anatase).

3.4. Atomic Force Microscopy (AFM)

The TiO_2 -SiO₂ thin films that were deposited on Corning glass are depicted in Figure 6 in both two- and three-dimensional AFM pictures. The surface morphologies of the films under study reveals porous structures that, interestingly, are characterized by different roughness. Figure 6a shows that $5TiO_2$ -9SiO₂ films are composed by monodisperse spherical particles of a diameter 3.683 nm with a mesoporous structure [37,38]. The main benefit of the reverse micellar route by hydrolysis of titanium isopropoxide to produce TiO_2 nanoparticles is monodispersity [39]. In this way, the hydration of surfactant polar heads by water molecules is in competition with the hydrolysis process. Growth restrictions and homogeneous particle sizes are caused by the surfactant molecule restructuring that surround the polar species produced during hydrolysis [37]. It is also observed from Figure 6b,c that the 7TiO₂-9SiO₂ and 9TiO₂-9SiO₂ thin films also have granular microstructures which are composed of ~4.53 nm and ~8.43 nm spheric crystals, respectively. AFM image analysis showed the values of surface roughness in addition to crystal diameter. The root mean square roughness values (R_{rms}) of 5TiO₂-9SiO₂, 7TiO₂-9SiO₂ and 9TiO₂-9SiO₂ correspond to 0.508, 0.177 and 0.076 nm, respectively.



Figure 6. 2- and 3-dimensional images of TiO₂-SiO₂ thin films with different numbers of layers. (**a**) 5TiO₂-9SiO₂ (5 layers), (**b**) 7TiO₂-9SiO₂ (7 layers), and (**c**) 9TiO₂-9SiO₂ (9 layers).

3.5. Scanning Electron Microscope (SEM)

Figure 7 shows the micrographs of thin films. The films under study were annealed at 550 °C; it was observed that the shapes of the formed grains appear to vary according to the number of layers. The most significant differences between the three samples were observed for five layers of TiO₂ (Figure 7a), seven layers (Figure 7b), and nine layers (Figure 7c). We observed that by increasing the thickness of the TiO2 films, crack formation did not take place, suggesting not only a relatively strong structure, but also that an increase in the film thickness did not lead to detachment of the deposited layers. For the $5TiO_2-9SiO_2$ thin film (Figure 7a), less closely packed TiO₂ particles were dispersed, and a sizable particle increase was observed. As the deposition of the layers in the $7TiO_2-9SiO_2$ sample

(Figure 7b) increased, densely packed and uniform nanoscale particles were observed; similar results have been reported in previous studies of TiO_2/SiO_2 films [40]. The image of the $9TiO_2-9SiO_2$ thin film (Figure 7c) shows an extremely smooth surface involving tiny and dense grains positioned on the surface of the film. These results are comparable to those mentioned by Binyu Yu et al. [41].





Figure 7. SEM pictures of: (a) sample 5TiO₂-9SiO₂; (b) sample 7TiO₂-9SiO₂; (c) sample 9TiO₂-9SiO₂.

3.6. High Resolution Transmission Electron Spectroscopy (HRTEM)

 7TiO_2 -9SiO₂ thin films were examined using High-resolution TEM (HRTEM) to evaluate their crystalline or amorphous. Size distribution analysis shown in Figure 8a reveals that the average diameter and standard deviation of 7TiO_2 -9SiO₂ nanoparticles on the surface of the film are about 3–5 nm—a value range that is not consistent with that calculated from XRD experiments. The Scherrer equation, however, is well known to produce a good approximation, and in this regard, the disordered wormhole-like pore structure of the dip-coating prepared sample was confirmed by TEM (see Figure 8b). This material is a good illustration of the type of molecular sieve in which the atomic organization is disordered similarly to amorphous or mesoporous silica, and the channel structure displays a disordered pattern of micropores with a high specific surface area. High-resolution TEM (HRTEM) images of 7TiO_2 -9SiO₂ in Figure 8c–e revealed the crystalline nature of the nanostructures under study with lattice fringe spacing of 3.52 Å, 1.48 Å, and 1.66 Å, respectively. These can be indexed to (101), (204), and (211) planes of anatase TiO₂-9SiO₂ sample. From

electron diffraction measurements, the interplanar distances (d) of 7TiO_2 -9SiO₂ samples were determined to be 2.33 Å, 1.33 Å and 1.16 Å. This result corresponds to anatase phase of TiO₂. The interplanar distance and the diffraction planes were identified using the powder diffraction files (PDF) #00-021-1272.



Figure 8. TEM micrography of sample 7TiO_2 -9SiO₂ (**a**) Size distribution of 7TiO_2 -9SiO₂ nanoparticles on thin films. (**b**) The disordered wormhole-like pore structure, (**c**-**e**) High-resolution TEM micrograph of 7TiO_2 -9SiO₂ thin films; crystalline planes are observed. This Figure shows the inter-planar distance obtained from various zones of the sample. (**f**) SAED pattern of 7TiO_2 -9SiO₂ thin films indexed using anatase TiO₂ crystallographic parameters.

3.7. Degradation of MB with SiO₂-TiO₂ Photocatalyst under UV Irradiation

The main by-products and most worrying pollutants in the textile industry are organic dyes, which are known to degrade when exposed to high levels of photocatalytic activity (PA) in mesoporous TiO₂. It is particularly important to consider a good excitation during photocatalysis, as the energy of the E_g must be exceeded. The TiO₂ anatase phase has an E_g of 3.2 eV, and the corresponding wavelength value of 387 nm showed that light with shorter wavelengths is needed for this project; a wavelength value of 254 nm was selected. TiO₂ is excited by UV radiation, resulting in valence band holes that oxidize OH⁻ ions or H₂O to produce the hydroxyl radical (·OH) species. The compound is an extremely potent oxidant that easily oxidizes most organic molecules, converting them to CO₂, water, and salts [42]. Nevertheless, to improve the absorption efficiency of the TiO₂, it must be hydrated with

some additive, such as P_2O_5 , carbon, or SiO₂ [43]. In this work we have deposited SiO₂ thin films on Corning glass substrates, subsequently, various layers of TiO₂ were deposited. The opportunity for the hydroxyl radical (·OH) and dye molecules to react during the PA can be enhanced if the thin films absorb more color molecules. The decision was made to utilize the photodegradation of MB to assess the PA of TiO₂-SiO₂ thin films for dye discoloration applications. UV/Vis spectroscopy was used to determine the solution's time-dependent MB concentration. Figure 9a plots the normalized MB concentration under UV radiation as a function of time in the absence of any photocatalyst, in the presence of SiO₂, and utilizing various concentrations of thin films. The ratio of C_t/C_0 at time t = 0 is calculated as 1, using C_0 as the initial MB concentration, and C_t corresponds to the concentration of unreacted dye at various times. Figure 9a clearly shows that while photolysis does not result in noticeable dye discoloration, MB concentration decreases roughly 20% after 5h for SiO₂ films, reaching substantially more extensive and faster discoloration performances when using TiO₂-SiO₂ films. Since 5TiO₂-9SiO₂ materials showed similar activity to that observed for $9TiO_2$ thin films (in which SiO_2 is not present) and since the photocatalytic activity of TiO_2 -SiO₂ increases as the number TiO_2 layers on SiO₂ is larger, it is possible to suggest that SiO2 acts not only as TiO2 support in these PA films but as a functional semiconductor layer in the hetero-semiconducting film. As observed from the data in Figure 9a, increasing the number of TiO₂ layers results in faster discoloration kinetic curves [44,45]. A detailed investigation of the function that particle size plays in pure TiO_2 photocatalysts under UV light (wavelength 310-330 nm) was made by Zhang et al. They discovered that the kinetics of the electron/hole recombination process depended critically on particle size [44]. According to Afshar et al., the challenges brought on by the drawbacks of pure titanium powder require the manufacture of modified titania. They found that an increased surface area and interaction regions between the SiO₂ and the titanium nanoparticles could result in a combined impact that can be the primary cause of the high activity of TiO_2 -SiO₂ [45].



Figure 9. (a) Normalized concentration of MB vs UV-light irradiation time in the presence of TiO₂-SiO₂ thin films. (b) Reaction kinetics of MB photocatalytic degradation at different loadings of TiO₂-SiO₂ catalyst.

In gas-solid systems, the Langmuir-Hinshelwood (L-H) model has been successfully used to explain the kinetics of heterogeneous catalysis. This model was expanded upon by Al-Ekabi and Serpone [46] to include heterogeneous catalysis of a liquid-solid system. In order to obtain quantitative information on the photocatalytic activity of the as-prepared products, the kinetics of photocatalytic degradation of MB was also investigated. The degradation of MB can be described using the pseudo-first-order Langmuir–Hinshelwood kinetic model as shown below:

$$r = -\frac{dC}{dt} = \mathbf{k}C^n \tag{5}$$

where C is the concentration of the solution, k is the reaction rate constant, and n is the order of the reaction. Since photocatalytic oxidation is governed by a first-order reaction, the Equation (6) is obtained:

$$-\frac{dC}{dt} = kC \tag{6}$$

Integrating the Equation (6), and using the following initial conditions, t = 0, $C = C_0$, $C' = \ln C_0$, we obtain the Equation (8) in which the reaction rate constant, k, allows for analysis of the efficiency of the dye degradation process.

$$-\ln C = \mathbf{k}t + C' \tag{7}$$

$$-\ln\left(\frac{C_t}{C_0}\right) = \mathbf{k}t\tag{8}$$

where the apparent first-order rate constant is denoted by k. With increasing TiO₂-SiO₂ catalyst loading, it was discovered that the rate constant k increased (Table 1). Multiple heterogeneous photocatalytic systems have used this kinetic model successfully. In Figure 9b, the curves for SiO₂ and TiO₂-SiO₂ with varied layers are presented as $-\ln(C_t/C_0)$ vs. *t*. In the presence of TiO₂, the SiO₂ thin films photocatalytic activity is enhanced [47]. SiO₂ thin films have the ability to become acidic, which increases the amount of surface hydroxyl groups [48]. Moreover, surface hydroxyl groups have the ability to take up photoinduced holes from TiO₂ to produce OH radicals, which can then oxidize absorbed molecules. Hence, Bronsted acidity can be mostly responsible for the increased TiO₂-SiO₂ activity, which is consistent with the earlier result by Lu et al. [49]. Simultaneously, it was found that the photocatalytic activity of SiO₂ could be significantly improved by depositing TiO₂ thin films on it. As seen in Figure 9b, photocatalysts made of 9TiO₂-9SiO₂ are substantially more active than SiO₂ at degrading MB.

Sample	k (h $^{-1}$)	R^2	Degradation (%)
9SiO ₂	0.048	0.997	21
9TiO ₂	0.406	0.982	82
5TiO ₂ -9SiO ₂	0.397	0.982	83
7TiO2-9SiO2	0.498	0.956	89
9TiO ₂ -9SiO ₂	0.978	0.993	98

Table 1. Results of the photodegradation of MB.

3.8. Photocatalytic Mechanism

Figure 10a shows a band diagram illustrating the energy levels of the conduction and valence bands for TiO_2 and SiO_2 . It is important to point out that the conduction band energy of TiO_2 is lower than that of SiO_2 ; therefore, photo-excited electrons on both semiconductor layers are readily transferred to the conduction band of TiO_2 . Inspection of the energy band positions and scheme in Fig 10 also shows that photo-generated holes are promoted to the valence band of TiO_2 where interphasial oxidation reactions may occur (in Figure 10b this hole-induced oxidation mechanism for methylene blue (MB) is depicted).



Figure 10. (a) TiO₂-SiO₂ Band diagram. ΔCB and ΔVB denote the conduction and valence band offset between SiO₂ and TiO₂, respectively, and E_F denote the Fermi level. (b) Photodegradation mechanism of TiO₂-SiO₂ under UV light irradiation.

In this way, when the photocatalyst absorbs a photon with energy equal to or greater than the band gap energy, the photogenerated electrons and holes are efficiently separated by the space-charge layer, with the holes being transported to the TiO_2 surface. The primary photon energy-derived elements that interact with H_2O or OH^- adsorbed on the surface to make $\cdot OH$ are called photogenerated holes [50–52]. As can be seen from Figure 10b and the equations that follow:

$$\mathrm{TiO}_2 + \mathrm{h}\nu \to \mathrm{h}^+ + e^- \tag{9}$$

$$h^+ + H_2 O \rightarrow \cdot OH + H^+ \tag{10}$$

$$h^+ + OH^- \rightarrow OH$$
 (11)

The superoxide radicals $(\cdot O_2^{-})$, which are highly oxidant species, are created when the photogenerated electrons interact with the O₂ on the surface. In fact, these reactions produce a variety of active free radicals with high oxidizing characteristics, such as $(\cdot OH, \cdot O_2^{-},$ and HOO·). It should be highlighted, too, that the high rate of photogenerated e⁻ h⁺ recombination makes less effective photodegradation of challenging contaminants. According to [53,54], the interaction between TiO₂ and SiO₂ improves the separation of charge carriers (e⁻ and h⁺) and makes it easier for them to transfer between one another. As a result, the suppression of electron-hole recombination is only partially effective, leading to an increase in photoactivity.

4. Conclusions

The TiO₂-SiO₂ thin films' structural, optical, and photocatalytic properties are synthesized and evaluated in this work, as well as the significance and importance of TiO₂ modified SiO₂ substrates. It has been demonstrated that TiO₂-SiO₂ thin films have high photocatalytic performance for the discoloration of Methylene Blue solutions, and likely for many diverse types of organic contaminants in aqueous effluents. The presence of the TiO₂ layers on top of SiO₂ thin films improved the photocatalytic properties of the films, due to the photo-generated electrons gathered in the TiO₂ conduction band and were drawn to the SiO₂ trap level, which inhibited the recombination of electrons and holes. The presence of nine layers of TiO₂ in the surface of SiO₂ yielded superior photocatalytic activity to the other samples. In the end, effective degradation of the model dye was achieved, which is crucial for the detoxification of water. In the future, by further controlling nanocrystals sizes and layers and mesopore sizes precisely, we can expect enhanced photocatalytic properties.

Author Contributions: Y.d.J.A.-S.: Conceived and designed the experiments, Research, Writing original draft. M.T.-A.: Analyzed and interpreted the data, analysis tools or data. S.G.-H.: Research, proofreading. L.A.G.: Proofreading, Supervision. A.M.-L.: Conceptualization, Research, Supervision, Proofreading and editing. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Data Availability Statement: The datasets used and/or analyzed during the current study are available from the corresponding author on reasonable request.

Acknowledgments: The authors would like to thank all members of the NanoBiotechnology and Photocatalysis Laboratory at Airport Campus of the Autonomous University of Querétaro.

Conflicts of Interest: The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Article Lattice Strain Relaxation and Compositional Control in As-Rich GaAsP/(100)GaAs Heterostructures Grown by MOVPE

Paola Prete^{1,*}, Daniele Calabriso², Emiliano Burresi³, Leander Tapfer³ and Nico Lovergine^{2,*}

- ¹ Institute of Microelectronics and Microsystems of CNR (IMM-CNR), Lecce Unit, Via Monteroni, I-73100 Lecce, Italy
- ² Department of Innovation Engineering, University of Salento, Via Monteroni, I-73100 Lecce, Italy; danielecalabriso.le@gmail.com
- ³ ENEA—National Agency for New Technologies, Energy and Sustainable Economic Development, Brindisi Research Center, Strada Statale 7 'Appia', I-72100 Brindisi, Italy; emiliano.burresi@enea.it (E.B.); Itapfer@yahoo.com (L.T.)
- * Correspondence: paola.prete@cnr.it (P.P.); nicola.lovergine@unisalento.it (N.L.)

Abstract: The fabrication of high-efficiency GaAsP-based solar cells on GaAs wafers requires addressing structural issues arising from the materials lattice mismatch. We report on tensile strain relaxation and composition control of MOVPE-grown As-rich GaAs_{1-x}P_x/(100)GaAs heterostructures studied by double-crystal X-ray diffraction and field emission scanning electron microscopy. Thin (80–150 nm) GaAs_{1-x}P_x epilayers appear partially relaxed (within 1–12% of the initial misfit) through a network of misfit dislocations along the sample [011] and [011] in plane directions. Values of the residual lattice strain as a function of epilayer thickness were compared with predictions from the equilibrium (Matthews–Blakeslee) and energy balance models. It is shown that the epilayers relax at a slower rate than expected based on the equilibrium model, an effect ascribed to the existence of an energy barrier to the nucleation of new dislocations. The study of GaAs_{1-x}P_x composition as a function of the V-group precursors ratio in the vapor during growth allowed for the determination of the As/P anion segregation coefficient. The latter agrees with values reported in the literature for P-rich alloys grown using the same precursor combination. P-incorporation into nearly pseudomorphic heterostructures turns out to be kinetically activated, with an activation energy E_A = 1.41 ± 0.04 eV over the entire alloy compositional range.

Keywords: GaAsP; III-V heterostructures; strain relaxation; critical thickness; metastable heterostructures; metalorganic vapor phase epitaxy; solid-vapor segregation coefficient; high-resolution X-ray diffraction; field emission scanning electron microscopy; III-V based solar cells

1. Introduction

Multi-junction (tandem) semiconductor solar cells in the form of stacked singlejunction cells, each absorbing a different interval of the solar spectrum, allow for external quantum efficiencies beyond the Shockley–Queisser limit for single-junction cells [1–3]. Tandem solar cells based on a crystalline silicon (Si) bottom junction are very attractive due to the relative low cost of Si. A dual-junction cell with a 1.7 eV top junction based on GaAsP and a Si (1.12 eV) bottom cell raises the theoretical power conversion efficiency (PCE) of the tandem cell above 30%. A common approach to the fabrication of such tandem cells is the direct monolithic growth of the III-V cell onto the Si bottom cell. However, structural constraints between III-V compounds and Si (e.g., the combined effects of lattice, thermal, and crystal polarity mismatches) limit the performances of such cells; despite the tremendous improvements in III-V/Si heteroepitaxy over recent years [4,5], solar PCEs remain far from theoretical figures [6,7].

Alternative approaches are being studied to overcome these limitations. Among others, the combination of a top cell based on free-standing III-V nanowires with a planar Si bottom

Citation: Prete, P.; Calabriso, D.; Burresi, E.; Tapfer, L.; Lovergine, N. Lattice Strain Relaxation and Compositional Control in As-Rich GaAsP/(100)GaAs Heterostructures Grown by MOVPE. *Materials* **2023**, *16*, 4254. https://doi.org/10.3390/ ma16124254

Academic Editors: Jose Maria De Teresa, Ricardo Lopez Anton and Sion Federico Olive Méndez

Received: 27 April 2023 Revised: 1 June 2023 Accepted: 5 June 2023 Published: 8 June 2023



Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). cell could guarantee higher efficiencies than their monolithic planar counterparts due to their potentially higher structural quality, as the lattice mismatch in these nanostructured cells can be accommodated more easily than in planar structures. In addition, nanowires have great potential as super-absorptive media for the fabrication of efficient solar cells [8]. Self-assembly of III-V nanowires on Si has been demonstrated [9] as well as tandem cells [10,11], while multiband absorption has been proposed using intermediate-band dilute-nitride III-V nanowires [12]. However, nanowire self-assembly is a complex process [13,14], and nanowire-based solar cells are still in an early stage of development.

Four-terminal tandem cells composed of a thin III-V planar cell mechanically stacked onto an interdigitated back contact Si cell with a glass interlayer have recently shown efficiency above 32.6% [15,16]. The advantage of such an approach is that the III-V top-cell could be monolithically grown on GaAs with higher quality: indeed, the 1.7 eV direct-bandgap GaAs_{0.775}P_{0.225} (As-rich) alloy has +8.18 \times 10⁻³ lattice misfit with GaAs, against the -2.28 \times 10⁻² of Si; similarly, the estimated RT thermal mismatch between GaAsP and GaAs is <3.8%, against values in the 110–118% range for GaAsP/Si heterostructures [17,18]. In addition, as-grown III-V structures are not affected by antiphase domains and rotational twins as in the heteroepitaxy on Si [4,19]. Chemical lift-off of the cell from the underlying GaAs and multiple re-utilization of the substrate have been demonstrated [20] as viable strategies to keep production costs low [21]. Wafer-bonded triple-junction III–V//Si solar cells with a PCE of 35.9% were also demonstrated by this approach [22].

Despite the abovementioned advantages of fabricating the GaAsP-based top-cell on GaAs, a compositionally graded GaAsP buffer is usually adopted between the substrate and the cell heterostructure to limit defect generation and propagation (e.g., threading dislocations, TDs) within the device. Indeed, GaAsP- and InGaAs-based metamorphic solar cells have been demonstrated on suitably step-graded GaAsP/(100)GaAs structures [23]. Low $(10^4-10^6 \text{ cm}^{-2})$ densities of TDs have been reported in GaAsP/(100)GaAs heterostructures grown by metalorganic vapor phase (MOVPE) [24] or molecular beam epitaxy [25]. Still, studies on the actual relaxation rate with thickness of single GaAs_{1-x}P_x (*x* < 0.5) epilayers on GaAs have never been published before in the literature.

This work reports for the first time on the lattice strain and plastic relaxation (misfit dislocation formation) of MOVPE-grown GaAs_{1-x}P_x/(100)GaAs heterostructures investigated by high-resolution double-crystal X-ray diffraction and field emission scanning electron microscopy (FESEM). The relaxation rate of present samples is estimated and compared with theoretical predictions; observations are explained in terms of dislocation nucleation. Furthermore, the As/P anion segregation coefficient for the GaAs_{1-x}P_x alloy is determined for our growth conditions and found to be in agreement with previous estimates at lower growth temperatures. The work will help to better understand the epitaxy of metamorphic step-graded GaAsP/(100)GaAs heterostructures as virtual substrates for the growth of high-efficiency GaAsP-based top solar cells.

2. Materials and Methods

GaAs_{1-x}P_x thin epilayers were grown on device-quality vertical gradient freeze (100)GaAs substrates (Wafer Technology, Milton Keynes, UK) by low (50 mbar) pressure MOVPE using an Aix 200RD reactor (Aixtron, Herzogenrath, Germany). Trimethylgallium (Me₃Ga), tertiary-butyl-arsine (^tBuAsH₂), and tertiary-butyl-phosphine (^tBuPH₂) (Dockweiler Chemicals, Marburg, Germany) were employed as Ga, As, and P precursors, respectively. Before loading into the reactor, the substrates were cleaned in isopropanol vapors for 1 h, etched in a H₂SO₄:H₂O₂:H₂O (4:1:2) solution for 8 min at around 40 °C, thoroughly rinsed in de-ionized water, and finally dried under pure N₂. In-situ annealing of the substrates was then performed for 10 min at 625 °C under a H₂ + ^tBuAsH₂ atmosphere to desorb oxides, organic residuals, and other contaminants from the GaAs surface. A thin (7 nm) GaAs epilayer was grown at the same temperature to reconstruct the substrate surface before GaAsP growth. Upon completion of the GaAsP epilayers

were grown under a fixed Me₃Ga molar flow of 12.3 µmol/min to ensure the same growth rate (~0.085 nm/s) for all samples. Different concentrations of V-group elements in the vapor were adopted to study the effects on GaAsP composition: the vapor stoichiometry $x_v = [^tBuPH_2]/([^tBuPH_2] + [^tBuAsH_2])$ was varied between 0.46 and 0.60, while the V:III ratio was fixed at 20:1 or 40:1. The growth time was in the 15–30 min range, so to obtain GaAsP thickness around one hundred nm.

The sample surface morphology was investigated by field-emission scanning electron microscopy (FESEM) in-plan observations using a Sigma VP (Zeiss, Oberkochen, Germany) microscope equipped with a Gemini-1 electron column and a primary electron beam energy of 20 keV. To this end, secondary (SE) or backscattered electron (BSE) signals were employed.

The microstructural properties of GaAs_{1-x}P_x alloy epilayers were investigated by X-ray diffraction. The measurements were carried out using an Empyrean diffractometer (Malvern-Panalytical, Malvern, UK) in a high-resolution double-crystal (HRDC) configuration. A Cu-target was employed as an X-ray source, and a 4-bounce Ge-crystal Bartels monochromator-collimator (symmetrical (220)-reflections) with an angular divergence of about 14 arcsec was employed as X-ray incidence optics. All measurements were carried out using a "wide open" PIXcel detector. The strain state and alloy composition of $GaAs_{1-x}P_x$ epilayers were determined by recording symmetrical and asymmetrical HRDC measurements in the vicinity of the (400) and (422) lattice points, respectively. In order to account for a possible offcut of the substrate surface or a tilt/rotation of the epilayer with respect to the substrate, all measurements were performed at four azimuthal angle settings (i.e., sample rotations about the surface normal), namely $\varphi = 0$, $\pi/2$, π , and $3/2\pi$, corresponding to the X-ray scattering plane along the in-plane $\langle 110 \rangle$ directions. For the asymmetric (422) reflection, the geometrical configuration with high incidence and glancing exit angles, i.e., direction cosines $\gamma_0 > |\gamma_h|$, was chosen because this configuration is very sensitive to in-plane strain components and lattice relaxation.

3. Results and Discussion

3.1. Determination of Lattice Strain and Alloy Composition of $GaAs_{1-x}P_x$ Epilayers from HRDC

Figure 1 shows the HRDC patterns around the symmetrical (400) and asymmetrical (422) reflections of two GaAs_{1-x}P_x/(100)GaAs heterostructures having different phosphorous mole fractions *x*. Patterns measured for the different azimuthal angles (not reported here) demonstrate that all epilayers are nearly pseudomorphic. Measured values of GaAs_{1-x}P_x lattice strain parallel to the (100) interface plane (ϵ_{\parallel}) are summarized in Table 1 for the studied samples. The lattice mismatch (*f*) and mole fraction *x* in the Table were calculated by using the relations of the second-order approximation for $\langle 100 \rangle$ -oriented zinc-blende heterostructures [26]. For the calculations, the lattice parameters and elastic constants of GaAs and GaP reported by Adachi [27] were used. The samples show different amounts of strain ϵ_{\parallel} and thus different degrees of plastic relaxation $\delta_{\parallel} \equiv (f - \epsilon_{\parallel})/f$ within the 1–12% range.

3.2. Observation of Defects-Related Features in $GaAs_{1-x}P_x$ Epilayers through FESEM

Figure 2a shows a FESEM surface micrograph of Sample C ($\delta_{\parallel} = 11.3\%$) obtained using SE imaging (sensitive to surface morphology); it shows the presence of mutually perpendicular (i.e., along the sample [011] and [011] in-plane directions) undulations of the epilayer surface, so-called cross-hatch morphology, observed in low-misfit GaAsP layers grown at relatively low temperatures [28]. The presence of cross-hatch is explained as the combination of strain relaxation by dislocation nucleation at surface steps (and their subsequent glide into the epilayer) and growth by surface step flow, which tends to smooth down the steps [29]. FESEM observations of the same surface region using BSE imaging show dense patterns of well-resolved mutually perpendicular dark lines (Figure 2b), corresponding (both in position and alignment) to the surface undulations in Figure 2a. As the samples are compositionally homogeneous and BSE imaging is less sensitive to surface features, these lines originate most likely from electron channeling contrast imaging (ECCI) associated with crystal defects (e.g., dislocations) [30–32]. Besides the surface cross-hatch, we observed the seldom occurrence of faceted trenches (FTs) (inset of Figure 2a) aligned along the $[01\overline{1}]$ direction with lengths varying between a few microns and several hundred microns. The latter have been associated with the formation of a micro-twin at the FT cusp [25]; interestingly, a strong BSE imaging contrast is observed in Figure 2b at a FT location. In comparison, BSE micrographs of Sample A (not reported here) show a negligible (although not null) density of dark lines, in agreement with the reduced plastic relaxation of this sample ($\delta_{\parallel} = 1.78\%$).



Figure 1. (a) Symmetrical (400) HRDC patterns recorded for two GaAs_{1-x}P_x/(100)GaAs heterostructures having GaAs_{1-x}P_x alloy composition x = 0.172 (sample A) and x = 0.266 (sample B). (b) Asymmetrical (422) HRDC patterns in the glancing exit setting, $\gamma_0 > |\gamma_h|$ (see inset), recorded for the same samples in (a). A schematic of the diffraction geometry is reported in the upper-left part of each panel.

Table 1. Composition (*x*) and elastic strain parallel to the hetero-interface (ϵ_{\parallel}) measured through HRDC for the investigated GaAs_{1-x}P_x/(100)GaAs heterostructures. Values of the epilayer thickness (*h*) and calculated lattice misfit (*f*) are also reported for each sample.

Sample	$GaAs_{1-x}P_x$ Thickness, <i>h</i> (nm)	x	Misfit, * <i>f</i> (×10 ⁻³)	Lattice Strain, * ϵ_{\parallel} (×10 ⁻³)
А	150	0.172	6.17	6.06
В	83	0.266	9.55	9.19
С	150	0.197	7.10	6.30

* Defined as $f = (a_{GaAs} - a)/a$ and $\epsilon_{\parallel} = (a_{\parallel} - a)/a$, where a_{GaAs} is the GaAs bulk lattice parameter, whilst a and a_{\parallel} are the GaAs_{1-x}P_x bulk and strained lattice parameters in the direction parallel to the heteroepitaxial interface, respectively.



Figure 2. Plan-view FESEM micrographs of Sample C recorded by using the microscope (**a**) SE and (**b**) BSE current signals. A short-faceted trench (FT) indicated by the arrow is observed in (**a**) and better visualized in the magnified micrograph shown in the inset. The same FT is observed as a few-micron long and narrow black segment in (**b**). White markers in the micrographs represent 4 µm.

3.3. Analysis of Epilayer Strain Relaxation

Figure 3a reports the $GaAs_{1-x}P_x$ thickness (Table 1) along with values of the critical thickness (h_c) for strain relaxation calculated based on the equilibrium theory of Matthews-Blakeslee [33] (Appendix A) as a function of alloy compositions. It appears that the epilayer thickness is beyond the corresponding h_c value, in qualitative agreement with the sample partial relaxation observed by HRDC. However, more compelling information on strain relaxation behavior in present heterostructures can be obtained by comparing the calculated Matthews–Blakeslee residual strain ϵ_{\parallel} for $h > h_c$ (Equation (A2)) with that measured in our samples as a function of the epilayer thickness, as shown in Figure 3b. The diagram clearly shows that the present epilayers are less plastically relaxed (metastable) than expected based on the equilibrium theory. This is a common experimental finding in mismatched heterostructures grown on high-crystalline-quality substrates (VGF-grown GaAs in our case), i.e., whenever the substrate TD density is not large enough to generate the required amount of plastic relaxation; new misfit dislocations must be then nucleated during the growth, a process limited by energy balance or kinetic barriers. The first case was proposed by People and Bean [34], who estimated the energy threshold for the generation of screw dislocations in a strained epilayer (Appendix A), despite the fact that such dislocations cannot relax elastic strain. Figure 3a reports the critical thickness for strain relaxation as a function of $GaAs_{1-x}P_x$ composition based on the People–Bean model (Equation (A3)): the as-estimated values of h_c appear indeed much larger than those calculated from Matthews-Blakeslee theory and well beyond the thickness of our partially relaxed epilayers. Plastic relaxation has been described by Marée et al. [35] in terms of surface nucleation and expansion into the epilayer of dissociated half-loops, taking into account the work done by the elastic stress field acting on expanding loops. This model was found to agree fairly well with experimental strain relaxation data in compressively-strained heterostructures [36].

For sufficiently thick epilayers, the observed dependence of the residual strain with thickness can be fitted by the semi-empirical power-law function

$$\epsilon_{\parallel}(h) = Ah^{-m},\tag{1}$$

where m = 1 for the Matthews–Blakeslee theory and m = 1/2 for the energy balance models [34,35] (Appendix A). The latter value is in good agreement with relaxation data for compressively strained metastable heterostructures [36,37]. Best-fitting of experimental data in Figure 3b with Equation (1) returned instead, a value $m = 0.671 \pm 0.046$ (i.e., $m \sim 2/3$). This finding suggests a relaxation rate behavior intermediate between that of Matthews– Blakeslee and the half-loop nucleation models; indeed, a larger proclivity toward plastic relaxation is expected for tensile-strained epilayers with respect to compressive ones.



Figure 3. (a) GaAs_{1-x}P_x thickness as function of alloy composition for the analyzed samples (blue points) and values of the critical thickness for plastic relaxation, calculated according to Matthews-Blakeslee (M&B) [33] and People-Bean (P&B) [34] (Appendix A). The percentage of plastic relaxation (δ_{\parallel}) is also indicated for each sample in the diagram. The dash-dotted red curve represents values of h_c^{eff} (see main text). (b) Lattice strain ϵ_{\parallel} as function of epilayer thickness for the measured samples (light blue points). Solid black line: expected values of $\epsilon_{\parallel}(h)$ according to M&B (Equation (A2)). The dashed horizontal lines represent the sample misfit values (Table 1). Dash-dotted red line in (b): Equation (1) with parameter values $A = 0.178 \pm 0.038$ and $m = 0.671 \pm 0.046$, best-fitting the experimental points.

Finally, we estimate the apparent critical thickness (h_c^{eff}) for strain relaxation of GaAsP/(100)GaAs heterostructures as a function of alloy composition by imposing the pseudomorphicity condition $\epsilon_{\parallel} = f$ to the quantity $\epsilon_{\parallel}(h)$ (Equation (1)) best fitting our experimental data. Figure 3a shows that the Matthews–Blakeslee h_c values lie below the h_c^{eff} curve, while all experimental points lie above it. Clearly, the h_c^{eff} curve represents an upper bound to epilayer pseudomorphicity in reason of the limited resolution (1×10^{-4}) of HRDC strain measurements; indeed, the absence of measurable strain does not imply that misfit dislocations are not present, as they would be generated as soon as the energy conditions allow it, that is, well before strain relaxation becomes appreciable. In this sense, electron microscopy observations (e.g., through ECCI) of individual dislocations are necessary to verify whether the onset of relaxation coincides with that of Matthews–Blakeslee or if it occurs at a larger thickness.

To date, studies on the structural properties of step-graded $GaAs_{1-x}P_x$ buffer layers for solar cell applications have predominantly focused on the evaluation of TD and FT densities as functions of the step compositional height and grading rate (i.e., the compositional change per unit thickness of the grown alloy): a lower grading rate was shown necessary with increasing x to maintain the density of FTs low and reduce the TD density [24,25]. However, no particular attention was paid to the actual strain relaxation within each of the buffer grading steps in those studies, despite the fact that the actual degree of plastic relaxation would affect the distribution of TDs throughout the final buffer layer. The present findings will help in further optimizing the structural properties of such step-graded GaAsP buffer layers, as well as in properly engineering strain-balanced InGaAs/GaAsP multiple quantum well structures as current-matched light-absorbing medium in monolithic triplejunction InGaAs/GaAs/Ge solar cells [38,39], ultimately leading to better performance III-V tandem solar cells.

Tensile-strained GaAsP layers also find applications in the fabrication of InGaAsP quantum well-based laser diode heterostructures on GaAs for NIR photon emission [40,41]. In this case, the use of an InGaAsP/InGaAsP/GaAsP active region allows for an effective

reduction of non-radiative recombination within the device and suppression of carrier leakage with respect to conventional AlGaAs/GaAs heterostructure laser diodes [42]. As the mechanism of degradation in a laser diode is related to the development of dark line defects associated with the generation and multiplication of misfit dislocations within the heterostructure active region, understanding GaAsP relaxation behavior is therefore critical in ensuring suppression/reduction of plastic relaxation within the proposed laser device structures.

3.4. Determination of the Solid-Vapor Segregation Coefficient for $GaAs_{1-x}P_x$

1

Figure 4a reports the solid-vapor distribution diagram for the analyzed GaAsP epilayers. It can be clearly observed that the P-composition x in the solid alloy is always below the corresponding content in the vapor (x_v) during the sample growth. The relative distribution of As and P between the two phases is described by the so-called segregation coefficient η defined as [43]

$$\eta = \frac{N_{As}/N_P}{[tBuAsH_2]/[tBuPH_2]}$$

where N_{As}/N_P represents the As to P anion concentration ratio in the GaAsP alloy and $[tBuAsH_2]/[tBuPH_2]$ is the corresponding precursor concentration ratio in the vapor. η has been shown to depend on the nature of the employed precursors and the growth temperature [43,44]. Furthermore, preferential As (P) segregation was observed for tensile (compressive) strained GaAsP epilayers with respect to fully relaxed ones, a compositional latching phenomenon ascribed to the different radii of As and P anions [28,45].



Figure 4. (a) Solid-vapor distribution diagram for the MOVPE growth of the GaAsP alloy at 600 °C: solid blue points represent experimental data; the red curve is the solid-vapor distribution curve (Equation (2)) best-fitting the experimental points with $\eta = 4.76 \pm 0.66$; (b) Arrhenius plot of $1/\eta$ as a function of the growth temperature: data are from the best-fitting value in (a) (solid blue point) and values reported in ref. [44] (solid black points).

As $x \equiv N_P / (N_P + N_{As})$, its value can be calculated for a given x_v composition of the vapor by the following expression:

$$x = 1/\left[\eta\left(\frac{1}{x_v} - 1\right) + 1\right],\tag{2}$$

if the actual value of η is known. We best-fitted the experimental points in Figure 4a with Equation (2) in order to determine η for our experimental conditions, which turned out to be 4.76 \pm 0.66. As η > 1, a preferential As incorporation in the GaAsP alloy occurs indeed in

our nearly pseudomorphic (tensile-strained) samples. Figure 4b allows us to compare our best-fitting η value with those estimated at lower growth temperatures by Chen et al. [44] for the same V-group precursor combination: the Arrhenius plot shows that the $1/\eta$ values align almost perfectly (regression coefficient R = 0.9985), indicating that P incorporation into the crystal is kinetically activated (i.e., increases with the growth temperature), with an apparent activation energy $E_A = 1.41 \pm 0.04$ eV, not far from that $(1.23 \pm 0.05 \text{ eV})$ estimated in ref. [44]. Noteworthy is also that very thin (20–40 nm) GaAs_{1-x}P_x (0.91 < *x* < 1.0) epilayers were employed by those authors for their estimation, indicating that the observed temperature dependence of η in Figure 4b holds across the entire compositional range.

4. Conclusions

We reported on tensile strain relaxation and composition control of MOVPE-grown $GaAs_{1-x}P_x/(100)GaAs$ heterostructures studied by HRDC X-ray diffraction measurements and FESEM observations. The strain values and alloy P-compositions were measured by HRDC, while FESEM observations proved the presence of misfit dislocations and their effect on the epilayer surface morphology. Thin (80–150 nm) $GaAs_{1-x}P_x$ epilayers appear partially relaxed through a network of misfit dislocations along the sample [011] and $[01\overline{1}]$ in-plane directions, giving rise to a cross-hatch surface morphology.

The relaxation rate as a function of epilayer thickness was compared with theoretical predictions from equilibrium (Matthews–Blakeslee) and energy balance models. It was shown that present epilayers relax at a slower rate than predicted by the equilibrium model, an effect ascribed to the existence of an energy barrier to the nucleation of new dislocations. A relaxation rate behavior intermediate between that of Matthews–Blakeslee and the half-loop nucleation models is proposed, although further data over a larger compositional interval are needed to confirm this finding.

The analysis of As-rich GaAs_{1-x}P_x alloy composition as a function of V-group precursors ratio and growth temperature allowed to determine the As/P anion segregation coefficient and compare it with previous reports in the literature. P incorporation into the crystal turned out kinetically activated, with an apparent activation energy $E_A = 1.41 \pm 0.04$ eV over the entire alloy compositional range.

The present results will help to optimize the design and growth of metamorphic GaAsP/(100)GaAs heterostructures as virtual substrates for the epitaxy of high-efficiency GaAsP-based solar cells and InGaAsP/InGaAsP/GaAsP-based NIR-emitting laser diodes.

Author Contributions: Conceptualization, N.L. and P.P.; methodology, N.L.; investigation, D.C., E.B., L.T., N.L. and P.P.; resources, L.T., N.L. and P.P.; writing—original draft preparation, L.T., N.L. and P.P.; writing—review and editing, L.T., N.L. and P.P.; visualization, L.T. and N.L.; supervision, N.L. and P.P.; funding acquisition, P.P.; project administration, P.P. All authors have read and agreed to the published version of the manuscript.

Funding: This research was supported by the Italian Ministry of University and Research (MUR) through the PON Project entitled "Bifacial Efficient Solar Cell Technology with 4-Terminal Architecture for Utility Scale (BEST4U)"—Project number: ARS01_00519.

Data Availability Statement: The data presented in this study are available on request.

Acknowledgments: The authors would like to acknowledge the expert support of Fabio Marzo during MOVPE growth experiments and FESEM observations.

Conflicts of Interest: The authors declare no conflict of interest. The funder had no role in the design of the study as well as in the collection, analysis, and interpretation of the data.

Appendix A

Plastic relaxation in strained heterostructures occurs through the generation of a network of dislocation lines (so-called misfit dislocations) lying on the epilayer/substrate interface plane; each misfit dislocation is supposed to be either (i) generated from the stretching and bending of pre-existing (i.e., in the substrate) TDs by the epilayer elastic stress field or (ii) nucleated anew during the epilayer growth. The two mechanisms have been alternatively employed in heterostructure relaxation models based on energy minimization or energy balance considerations, respectively.

According to Matthews–Blakeslee equilibrium theory [33], the critical thickness (h_c) for the onset of plastic relaxation in mismatched heterostructures can be calculated upon minimization of the epilayer total (elastic and plastic) areal energy density, assuming the misfit dislocations are generated by mechanism (i) above, resulting in the equation

$$h_c = \frac{b}{4\pi f \cos \lambda} \left(\frac{1 - \nu \cos^2 \lambda}{1 - \nu} \right) [1 + \ln(h_c/b)],\tag{A1}$$

where ν is the Poisson ratio of the epilayer crystal (for GaAsP alloys, $\nu \approx 0.31$ [46,47]), *b* is the Burger vector of the misfit dislocations, and λ is the angle between the Burger vector and the normal to the dislocation line. For thickness values $h < h_c$ the minimal energy is obtained for fully pseudomorphic epilayers ($\epsilon_{\parallel} = f$), while for $h > h_c$ plastic relaxation is possible and the elastic strain shall decrease according to the expression

$$\epsilon_{\parallel}(h) = \frac{b}{4\pi\hbar\cos\lambda} \left(\frac{1-\nu\cos^2\lambda}{1-\nu}\right) [1+\ln(h/b)]. \tag{A2}$$

It appears from Equation (A2) that for large thickness $(h/b \gg 1)$ one obtains $\epsilon_{\parallel}(h) \sim h^{-1}$. In (100)-oriented semiconductor heterostructures, plastic relaxation occurs mostly through a network of 60°-mixed perfect dislocations along [011] and $[01\overline{1}]$ in-plane directions, having Burger vectors $\overrightarrow{b} = \frac{a}{2}\langle 011 \rangle$ (*a* being the epilayer lattice parameter), their edge-component parallel to the epilayer/substrate interface being $b_{\parallel} = b \cos \lambda$, and $\lambda = 60^{\circ}$. Given the heterostructure misfit *f*, the critical thickness h_c and elastic strain $\epsilon_{\parallel}(h)$ can be readily calculated from Equations (A1) and (A2), respectively.

Alternative relaxation models have been proposed to estimate the critical thickness in mismatched heterostructures based on energy balance considerations [34,35]. In the People–Bean model, misfit dislocations are generated when the areal elastic energy density of the strained epilayers exceeds the energy density required for the generation of a screw dislocation at the epilayer/substrate hetero-interface; the critical thickness h_c can be then estimated by solving the equation [34].

$$h_c = \frac{1}{16\pi\sqrt{2}a(x)} \left(\frac{b}{f}\right)^2 \left(\frac{1-\nu}{1+\nu}\right) \ln(h_c/b),\tag{A3}$$

where a(x) is the epilayer lattice parameter, and the other symbols have the same meaning as above. For $h > h_c$ plastic relaxation is expected, and the elastic strain decreases according to the expression

$$\epsilon_{\parallel}(h) = \frac{b}{4\pi\sqrt[4]{2}} \sqrt{\frac{\pi}{a(x)}} \left(\frac{1}{h}\right) \left(\frac{1-\nu}{1+\nu}\right) \ln(h/b)$$

For large thickness values, this again leads to $\epsilon_{\parallel}(h) \sim h^{-1/2}$. The same functional dependence is obtained by the half-loop dislocation nucleation model [35].

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Article TiNbN Hard Coating Deposited at Varied Substrate Temperature by Cathodic Arc: Tribological Performance under Simulated Cutting Conditions

Juan Manuel Gonzalez-Carmona^{1,*}, Claudia Lorena Mambuscay², Carolina Ortega-Portilla¹, Abel Hurtado-Macias³ and Jeferson Fernando Piamba^{2,*}

- ¹ CONAHCYT-Centro de Ingeniería y Desarrollo Industrial (CIDESI), Av. Playa, Av. Pie de la Cuesta No. 702, Desarrollo San Pablo, Santiago de Querétaro 76125, Mexico; iortega@posgrado.cidesi.edu.mx
- Facultad de Ciencias Naturales y Matemáticas, Universidad de Ibagué, Carrera 22 Calle 67, Ibagué 730002, Colombia; claudialorena0524@gmail.com
- ³ Centro de Investigación en Materiales Avanzados, S.C., Laboratorio Nacional de Nanotecnología, Miguel de Cervantes 120, Complejo Industrial Chihuahua, Chihuahua 31109, Mexico; abel.hurtado@cimav.edu.mx
- Correspondence: juan.gonzalez@cidesi.edu.mx (J.M.G.-C.); jeferson.piamba@unibague.edu.co (J.F.P.); Tel.: +52-4427480070 (J.M.G.-C.); +57-313-699-8153 (J.F.P.)

Abstract: This study focused on investigating the adhesion and tribological properties of niobiumdoped titanium nitride (TiNbN) coatings deposited on D2 steel substrates at various substrate temperatures (Ts) under simulated cutting conditions. X-ray diffraction confirmed the presence of coatings with an FCC crystalline structure, where Nb substitutes Ti atoms in the TiN lattice. With increasing Ts, the lattice parameter decreased, and the crystallite material transitioned from flat-like to spherical shapes. Nanoindentation tests revealed an increase in hardness (H) with Ts, while a decrease in the elastic modulus (E) resulted in an improved elastic strain limit for failure (H/E) and plastic deformation resistance (H^3/E^2), thereby enhancing stiffness and contact elasticity. Adhesion analysis showed critical loads of ~50 N at Ts of 200 and 400 °C, and ~38 N at Ts of 600 °C. Cohesive failures were associated with lateral cracking, while adhesive failures were attributed to chipping spallation. The tribological behavior was evaluated using a pin-on-disk test, which indicated an increase in friction coefficients with Ts, although they remained lower than those of the substrate. Friction and wear were influenced by the surface morphology, facilitating the formation of abrasive particles. However, the absence of coating detachment in the wear tracks suggested that the films were capable of withstanding the load and wear.

Keywords: wear; arc PVD; tribology; adhesion

De Teresa, Ricardo Lopez Anton and Sion Federico Olive Méndez 1.

Received: 26 May 2023 Revised: 17 June 2023 Accepted: 17 June 2023 Published: 22 June 2023

Citation: Gonzalez-Carmona, J.M.; Mambuscay, C.L.; Ortega-Portilla, C.;

Hurtado-Macias, A.; Piamba, J.F.

TiNbN Hard Coating Deposited at

Varied Substrate Temperature by

Cathodic Arc: Tribological

ma16134531

Performance under Simulated

Academic Editors: Jose Maria

Cutting Conditions. *Materials* 2023, 16, 4531. https://doi.org/10.3390/



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1. Introduction

The surface of a material refers to the external part of a body that comes into contact with the environment, where wear and corrosion can occur [1]. These phenomena pose significant challenges for industry as components of industrial machinery can be damaged, resulting in production stoppages for the replacement of worn-out and corroded components, leading to losses in time and money [2,3]. To address these challenges, industries seek continuous improvement and production time reduction employing new durable materials that optimize production processes effectively and efficiently [3–5]. In this regard, the deposition of thin-film has become increasingly popular in recent years due to the high demand generated in the industry. These coatings enhance the surface properties of the substrate, providing high hardness, low coefficient of friction, resistance to wear and corrosion especially in chemically aggressive environments, thereby increasing its lifespan and expanding its range of applications [2–6].

Adhesion is one of the most critical properties of a coating/substrate system as it determines the life cycle of the film. Various qualitative and quantitative techniques are

available to assess adherence. Qualitative techniques involve determination of the behavior of surface cracks generated by an indentation, while quantitative methods seek to obtain the critical loads, both adhesive and cohesive, using dynamic scratching [7]. However, adhesion depends on intrinsic parameters, such as the relationship between the film and substrate hardness, the interface and diffusion type, morphology, and roughness. These factors make adhesion evaluation complex, requiring in-depth quantitative and qualitative analysis of the failure mechanisms of surfaces [8]. Similarly, the tribological properties indicate the material's possible applications during contact and relative motion with another surface and depend on intrinsic parameters similar to those of adhesion, with the addition of tribo-oxidation, particle formation, and the counterpart's material [9]. Friction mechanisms are associated with the simultaneous occurrence of adhesion and abrasion processes. The dominance of either of these components depends on the surface characteristics. However, the coefficients of friction and wear undergo changes over time. In the initial stages of motion, friction and wear are primarily influenced by the contact between surface asperities. These asperities undergo cyclic deformation and strain hardening. When this process becomes critical, the asperities fracture, leading to the formation of particles. These particles then undergo a cyclic process of deformation, hardening, and fracturing. As the particles reach a critical size, they are expelled from the wear track, leaving the surface exposed, thus initiating the process anew. However, if the particles possess high hardness and a spherical geometry, they can withstand the contact load and contribute to thirdbody friction, reducing the coefficient of friction. Conversely, if the particles adhere to the surface, they can give rise to abrasive mechanisms such as scratching and ploughing. In the advanced stages of friction, a steady state is achieved where the coefficient of friction stabilizes. During this stage, the average number of particles formed is equivalent to the number of particles leaving the track, resulting in the surface tending towards a polished state [7,9–11]. Titanium nitride (TiN) is a material that can be synthesized using physical vapor deposition (PVD) and is widely used due to its mechanical, tribological properties, and corrosion resistance. However, its usage is limited at high temperatures since it tends to form titanium oxide (TiO₂) in air at operating temperatures above 600 $^{\circ}$ C. This phenomenon generates detachment of the film and an increase in wear due to oxidation and tribo-oxidation [3,5,12]. Niobium nitride (NbN) has been used in industry due to its wear resistance, chemical and thermal stability, and high shear strength at temperatures between 800 °C and 1000 °C [3,13–17]. Studies have shown that TiN/NbN multilayer coatings have a hardness range of 23 to 28 GPa, which decreases at temperatures above 800 °C but maintains a higher value compared to their monolayers (TiN and NbN) [18–20]. Considering the need to develop coatings with increased wear and corrosion resistance, ternary compounds, such as titanium niobium nitride (TiNbN), combine the properties mentioned above. These coatings provide better adhesion at the film/substrate interface, increased thermal stability and wear resistance, enabling them to reach high operating temperatures [21-23].

Deposition of TiNbN has been reported with equiaxial and semi-columnar grains, with a face-centered cubic (FCC) crystalline structure. The atomic radii of Nb and Ti are similar, and thus Nb atoms replace Ti atoms in the TiN structure. However, small differences in radius increase the compressive stresses of the material, enhancing its mechanical properties compared to TiN [24,25]. The available literature indicates that the mechanical properties of the material depend on the chemical composition of the coating, specifically the percentage of Nb, as well as on the film's morphology, which, in turn, is dependent on the deposition technique. Hardness measurements have shown values ranging between 10 and 26 GPa for values above 25% Nb [25–27]. However, there is currently no available information, to the best of our knowledge, on the mechanical properties of TiNbN coatings with low Nb percentages. Although reports on the tribological properties have been explored under low load, low speed, and short distance conditions, showing a coefficient of friction of approximately 0.1 and wear rate of approximately 10⁻⁴ mm³/Nm. Abrasion and the

formation of hard particles are the main reported wear mechanisms [25,28]. Thus, there is a significant information gap in the information available, and studies are necessary to determine the adhesion, mechanical, and tribological properties of TiNbN coatings under severe wear conditions simulating cutting tool environments, for example. The design of protective coatings offers a means to enhance the longevity of various tool types. However, the existing information regarding the mechanical and tribological behavior of TiNbN coatings fails to demonstrate advancements in their application as surface protection for diverse cutting tools. Considering the material's favorable mechanical properties and chemical stability, it possesses ideal characteristics for this purpose. Consequently, it is crucial to ascertain the extent of this material's applicability as a protective coating in simulated cutting environments and to evaluate its tribological properties for suitability. Therefore, this work studied the mechanical properties, adhesion, and tribological properties of TiNbN coatings deposited by cathodic arc, varying the substrate temperature (Ts) to study their resistance in severe wear environments, simulating conditions similar to those of cutting tools.

2. Materials and Methods

2.1. Sample Preparation

A cylindrical bar, made of AISI D2 steel, with a diameter of 2.5 cm and a length of 100 cm, was cut into cylinders of 7 mm thickness. These cylinders were then subjected to thermal treatment, involving quenching at 1000 °C and followed by cooling in water. They were further subjected to double tempering at 400 °C and cooled in air. Subsequently, the steel surface was prepared according to the ASTM E3-11 standard [29], using a series of silicon carbide (SiC) abrasive papers with increasing grain sizes, ranging from 80 to 2500. Finally, the surface was polished to a mirror finish using 0.1 μ m diamond paste.

2.2. Coating Deposition

Prior to deposition, the substrates underwent ultrasonic cleaning in alcohol for 15 min, using a 45 kHz sweep frequency in an Elmasonic X-tra US 550 ultrasonic bath (Elma Schmidbauer Gmbh, Singen, Germany). They were then mounted onto a 2-fold rotation substrate holder with a rotation frequency of 2 Hz. TiNbN coatings were then deposited onto silicon (Si) and D2 steel substrates using an Oerlikon Domino Mini Arc-PVD equipment (Oerlikon, Zürich, Switzerland) [9]. Two titanium cathodes with a diameter of 7.62 cm and a purity of 99.995% were used, each with a niobium insert (diameter of 1.27 cm and a purity of 99.99%), which comprised $\sim 1\%$ of the cathode surface. Deposition conditions are presented in Table 1. Coatings were deposited at different substrate temperatures (Ts), specifically 200 °C, 400 °C, and 600 °C, to observe their effects on the adhesion, mechanical, and tribological properties of the surface. The substrates were heated using resistors connected to a 6 kW source, and the temperature was controlled using an Impac 140 infrared pyrometer and three thermocouples located in the sample holder. The deposition process started once the temperature stabilized at the desired value for 60 min. The conditions were optimized to achieve coatings with average thicknesses of 5 μ m within a deposition time of ~60 min. Prior to deposition, plasma cleaning was performed using Ar gas for 20 min at a pressure of 0.4 Pa (with a flow rate of 278 sccm) and a pulsed bias voltage of -50 V (at a frequency of 80 kHz with 80% duty cycle).

Table 1. Coating d	eposition c	onditions.
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Pressure (Pa)	Nitrogen Flow (sccm)	Power (kW)	Bias Voltage (V)	Temperature (°C)
0.4	500	3	-100	200 400 600

2.3. Coating Characterization

To determine the crystalline structure, X-ray diffraction (XRD) was carried out using a Rigaku SmartLab diffractometer (Rigaku, The Woodlands, TX, USA) with CuK α radiation ($\lambda = 1.5406$ nm) at a grazing incidence angle ($\Omega = 1.5^{\circ}$). The patterns were collected from 20 to 90° in steps of 0.04° for 3 s/step. A Rietveld refinement was then performed for crystallographic analysis to obtain the lattice parameters and crystallite size. For the determination of thickness, chemical composition, and surface morphology, both scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) were utilized. These analyses were conducted using a Jeol JSM-7200F FE-SEM microscope (Jeol, Tokyo, Japan) equipped with an Oxford ULTIMAX 100 EDS probe (Oxford Instruments, Abingdon, UK).

To measure roughness, a BRUKER DktakXT 100 contact profilometer (Bruker, Billerica, MA, USA) was employed with a contact load of 3 mg and a 4 mm distance. Eight measurements were taken in different sections of the surface and averaged. Nanoindentation tests were performed using a Hysitron TI 700 UBI equipment (Bruker, Billerica, MA, USA) with a 1 mN load and a 3-faced pyramidal Berkovich indenter. Load–displacement curves were analyzed using the Oliver and Pharr method with a 3 \times 3 indentation matrix. Corrections were made for compliance and contact area function using a fused silica reference standard. Vickers hardness was measured in accordance with the ASTM E92-17 standard [30] using a pyramidal-type diamond indenter with a 136° angle between the faces and an applied load of 10 N. Three indentations were made with a dead time of 12 s.

To evaluate the adhesion of the coating to the substrate, scratch tests were conducted in accordance with the ASTM C1624-05 standard [31] using a Rockwell C indenter (200 μ m). The tests involved applying a normal load ranging from 0.1 to100 N over a 5 mm distance at a speed of 7 mm/min. SEM images were taken of the areas where cohesive and adhesive failures occurred. Micro-indentation and dynamic scratching were performed using an Anton Paar Revestest (RST3) equipment.

For the determination of the material's tribological properties, Pin-On-Disk tests were carried out using an Anton Paar THT1000 tribometer, following the ASTM G99-17 standard [32]. The tests were conducted with a 6 mm diameter alumina counterpart (Al₂O₃) under a normal load of 5 N, a linear speed of 8.50 cm/s for 5000 cycles (~100 m), and a 3 mm radius. The wear rate (k) was determined using the Archard model (k = V/Ld), where V represents the wear volume obtained by contact profilometry, L is the load, and d is the distance of the tribology test [32].

3. Results and Discussion

3.1. Crystalline Structure and Chemical Composition

The analysis conducted by XRD (Figure 1a) revealed an FCC crystalline structure with an Fm3m space group. Regardless of Ts, all diffractograms showed a peak shift towards higher diffraction angles compared to the position of the TiNbN phase peaks (black lines on the bottom) (see Figure 1b). This shift is more pronounced at higher angles and can be attributed to a combined effect of Nb inclusion within the TiN lattice (resulting from differences in atomic radii, Ti = 176 pm and Nb = 198 pm) and the generation of internal stress in the thin film due to the increase in Ts. All patterns displayed a monophasic structure (TiNbN) with average calculated lattice parameter (*a*) of 4.31 Å (see Table 2). Since Nb replaces Ti atoms in the TiN crystal lattice, the obtained lattice parameter falls between the values reported for nitrides (TiN = 4.12 A and NbN = 4.37 A) [33,34].

However, the reduction of the lattice parameter with respect to Ts, as observed in Table 2, indicates the formation of compressive stresses in the structure. This phenomenon is associated with the increase in density with higher substrate temperatures [22]. These results also indicate complete solubility between TiN and NbN, which is consistent with findings from other studies in the literature [22,25,28].



Figure 1. (a) X-ray diffraction of coatings deposited at Ts 200 (red), 400 (Blue), and 600 °C (green), (b) zoom of the peaks (111) for the different temperatures.

Table 2. Structural and composition results of coatings of TiNbN at different temperatures; *a* indicates the lattice parameter, φ L perpendicular and φ || parallel crystalline size.

Ts (°C)	$a~(\pm 0.02~{ m \AA})$	φL (± 0.1 nm)	$\phi \parallel$ (\pm 0.1 nm)
200	4.35	72.1	11.0
400	4.34	52.5	18.3
600	4.24	41.4	27.3

The results for crystallite size (Table 2) suggest that the coherent zone is larger, perpendicular (φ L) to the incident X-rays compared to parallel (φ ||) orientation. This finding suggest that the crystallite shape is flat-like for low Ts. However, as the temperature increases, the crystals tend to adopt a spherical shape. This transition indicates an improvement in the packing of the crystalline domains within the material as the temperature rises, resulting in smaller crystallographic domains with spherical geometries [22].

The chemical composition of each film is presented in Table 3. An increase in substrate temperature resulted in a decrease in titanium (Ti) content compared to nitrogen (N), while the quantity of niobium (Nb) remained relatively constant. These findings suggest a reduction in the adsorption of Ti atoms due to the elevated substrate temperature [35]. However, the N/Ti ratio increased as the substrate temperature increased, indicating an enhanced reactivity between these two elements [36]. The maximum value of the N/Ti ratio reached 0.99 at a Ts of 600 °C.

Table 3. Chemical composition and coating thickness.

Ts (°C)	Ti (at%)	Nb (at%)	N (at%)	Thickness (µm)
200	57.86 ± 7.28	0.21 ± 0.01	41.93 ± 7.27	4.68 ± 0.03
400	51.06 ± 0.57	0.18 ± 0.02	48.76 ± 0.58	6.80 ± 0.12
600	44.72 ± 3.09	0.15 ± 0.02	55.12 ± 3.08	5.93 ± 0.04

3.2. Morphology, Thickness, and Roughness

The surface morphology of the films, as depicted in Figure 2, reveals the presence of droplets and pores, which are characteristic features of the cathodic arc deposition process (Figure 2a–c). These surface characteristics significantly influence the mechanical and tribological properties of the surface, as they act as stress concentrators, impacting crack behavior. Cracks can initiate or propagate around sub-micron-sized defects and can be associated with droplets of micrometric sizes [22,36–39]. The cross-sections of the coatings, illustrated in Figure 2d–f, display a dense columnar growth pattern typical of ceramic coatings such as TiN. However, this growth pattern is interrupted by the presence of molten material droplets that are expelled from the cathode and become embedded in the coating, resulting in the formation of pinholes [22,35,38,40].



Figure 2. SEM images of the coating surface deposited at different substrate temperatures Ts: (a) 200 °C, (b) 400 °C, (c) 600 °C and cross-section of the coatings deposited using (d) 200 °C, (e) 400 °C, and (f) 600 °C.

Table 4 presents the average roughness (Ra), root mean square roughness (Rq), and the Rq/Ra ratio for the substrate and coatings deposited at different Ts. The surface and crosssectional profile analysis (see Figure 2) revealed the presence of microdroplets and pores, which contribute to increased roughness values in the coatings compared to the substrate. However, both Ra and Rq decrease with increasing substrate temperature. This can be attributed to the increase in the mobility of the adatoms at higher temperature, leading to the formation of denser coatings, with fewer defects [22]. The Rq/Ra ratio indicates that, regardless of Ts, the roughness distribution tends to be random, with characterized peaks and valleys. This is a result of the initial mechanical polishing performed on the surfaces before deposition and the subsequent formation of droplets and pores.

Table 4. Roughness of the D2 steel and TiNbN coatings.

Ts (°C)	Ra (nm)	Rq (nm)	Rq/Ra
D2 Steel	64.27 ± 24.05	78.67 ± 26.44	1.24
200	358.70 ± 261.26	702.12 ± 417.52	2.04
400	141.27 ± 38.66	263.91 ± 85.39	1.85
600	179.33 ± 33.96	340.78 ± 77.81	1.89

As mentioned in the experimental details, the process parameters were standardized to achieve an approximate coating thickness of 5 μ m. However, it is important to note that the cathodic arc deposition technique may introduce slight deviations from the expected thickness. This variation can be attributed to the random nature of the arc when it interacts with the cathode surface. The arcs move across the surface, generating cathodic spots and causing material evaporation. However, it is not possible to precisely predict the location where the arc will strike, resulting in fluctuations in evaporation and deposition rates. These variations are particularly influenced by the compaction density and surface quality of the cathode. Over time and with an increase in the final thickness of the coating, this phenomenon becomes more noticeable [41,42].

3.3. Mechanical Properties

Figure 3a shows the load vs. displacement curves for of the TiNbN coatings for the different Ts. No defects, such as pop-ins, were observed in the curves, indicating the absence of crack formation during the loading stage of the surface deformation process [43,44].

However, increasing the substrate temperature reduces the maximum penetration of the indenter, implying an increase in hardness. Figure 3b shows the hardness (H) values as a function of Ts. A slight increase in H is observed with higher Ts, ranging between ~29 and ~32 GPa. This effect is primarily attributed to the increase in compressive stresses within the coatings, which stem from differences in the coefficient of thermal expansion between the film and the substrate, as well as disparities in the atomic radii of Ti and Nb. These consequences were analyzed by XRD, which revealed shifts in the peaks towards higher diffraction angles (Figure 1b). Additionally, an increase in temperature is expected to enhance density [45].



Figure 3. Mechanical properties obtained by nanoindentation. (a) Representative load–displacement plot for different Ts, (b) hardness and elastic modulus, and (c) elastic strain limit for failure (H/E) and plastic deformation resistance (H^3/E^2).

On the contrary, the average value of the elastic modulus (E) (Figure 3b) decreases with increasing temperature, resulting in the increase of the coefficients H/E (elastic strain limit for failure) and H^3/E^2 (plastic deformation resistance) with Ts (Figure 3c). However, the statistical distribution of data obtained for E indicates that the coatings exhibit similar values for different Ts. Consequently, when considering the propagation of statistical deviation, the value of H/E does not show a significant change as a function of Ts. These results suggest that more energy is required for the generation of sudden cracks, and the initial contact tends to be more elastic [43,44]. As observed in the chemical composition analysis, increase in the atomic percentage of nitrogen (see Table 3) and hardness were observed with increasing temperature. This is attributed to the greater number of covalent bonds, which are stronger than metallic bonds [46]. Furthermore, the average increase in H/E and H³/E² implies a more rigid crystal structure upon contact. A similar phenomenon has been observed in other transition metal nitrides [27,47].

3.4. Adhesion

The adhesion of the coatings was determined by dynamic scratch tests. Table 5 shows the critical loads of cohesion (Lc1) and adhesion (Lc2), calculated from the drag coefficient, acoustic emission, and load vs. distance plots. These values were averaged from three separate measurements. Figure 4 shows an overview of the scratch tracks and

SEM images of the sections from the scratch track where critical loads were obtained. A decrease in Lcs was observed with increasing substrate temperature. As discussed in the structural, morphological, and mechanical properties sections, the increase in compressive stresses with Ts also leads to an increase in the rigidity of the coatings. This rigidity enhances the generation of cracks and the detachment of coating material with high stresses, resulting in decreased adhesion, despite the improvement in the mechanical properties of the system [27,45]. The observed increase in hardness (Figure 3b) does not guarantee improve adhesion. A harder coating is generally less prone to scratching or removal from the substrate, indicating better adhesion. However, the slight reduction in elastic modulus (Figure 3b) and the increase in plastic deformation resistance (Figure 3c) generally lead to a reduction in the resistance to crack initiation and propagation at the film/substrate interface [27,35,44]. This indicates that the stresses generated at the substrate/film interface play a crucial role in coating design and that increasing the mechanical properties of the surface must be balanced with the formation of coherent interfaces during deposition.



Figure 4. Overview of the scratch tracks and SEM images of the failures on the critical load obtained from the scratch test for the coatings deposited at different Ts.

Ts (°C)	Lc1 (N)	Lc2 (N)
200	36.9 ± 0.18	53.63 ± 0.27
400	22.55 ± 0.11	48.57 ± 0.24
600	18.45 ± 0.09	38.45 ± 0.19

Table 5. Critical load obtained from the scratch test.

However, on demonstrating the repeatability of the scratch test, similar failure types were observed regardless of the substrate temperature. Figure 4 shows an overview of the scratch tracks and SEM images of the cohesive (Lc1) and adhesive (Lc2) failures for the different substrate temperatures. The cohesive failures observed correspond to lateral cracks, which are micro-cracks occurring at the edges of the track that opens parallel to the scratch direction. Additionally, the coating deposited at Ts = $400 \,^{\circ}$ C shows conformal cracks, forming arcs that open away from the direction of scratching. These cracks generates because the film tries to conform to the plastic deformation of the substrate. On the other hand, adhesive failures were related to chipping spallation, resulting in rounded removal regions of coating extending laterally from the edges of the track. The film deposited at Ts = 600 °C displays adhesive cracks that form perpendicular to the scratch direction, originating from the adhesive failures (chippings). These cracks develop at the interface between the film and the substrate and are more common in brittle coatings with high thicknesses. This observations aligns with the analysis conducted on the mechanical properties, where this particular coating exhibits the highest hardness and the lowest elastic modulus among the entire set.

The dynamic scratch analysis performed showed that at lower substrate temperatures, higher adherence was observed, accompanied by less severe failures, as observed in the case of Ts = 200 °C. In contrast, higher substrate temperatures resulted in cohesive and adhesive failures occurring at lower loads. This behavior is attributed to the lower plastic deformation resistance of the film (Figure 3c), allowing it to accommodate the substrate deformation and leading to adhesive failure at higher loads.

Furthermore, an increase in substrate temperature enhances the mobility of species within the substrate. This increased mobility leads to stabilization in higher energy sites, which can either improve or worsen the adhesion forces. Therefore, the temperature increase is associated with higher energy accumulation at the interface, facilitating the thermal diffusion of the coating towards the substrate. Additionally, elevated substrate temperatures contribute to the generation of compressive stresses, which can have a negative impact on adhesion [22,48,49].

3.5. Cracking Patterns

Figure 5 presents the images of the Vickers indentations created on the coated surface. The presence of roughness, pores, and microdroplets (as shown in Figure 2), along with variations in compressive stresses throughout the thickness and the accumulation of elastic energy in the coating due to increasing substrate temperature, contribute to induced failures in the material. These failures manifest as cracks parallel to the edges of the indentation (referred to as picture frame cracking) and partial delamination of the coating. Picture frame cracking occurs due to the plastic deformation of the steel, which causes the coating to bend [50,51] These failures may also originate from pores or pinholes formed during the deposition process.

Considering the mechanical properties of the surfaces, where the hardness and plastic deformation resistance of the film exceed those of steel, the formation of picture frame cracking on the deformed surface is expected, as previously observed in TiN coatings [50]. Additionally, the variation in substrate temperature leads to the release of elastic energy stored within the coatings, resulting in cracks propagating across the interface and ultimately causing coating detachment [52].



Figure 5. Indentation images at 10 N of TiNbN coating deposited at (**a**) Ts = 200 °C, (**b**) Ts = 400 °C, and (**c**) Ts = 600 °C.

Edge cracks were observed in the coatings deposited at substrate temperatures of 400 °C and 600 °C (Figure 5b,c respectively). This type of failure occurs when there is an increase in compressive stresses, allowing the crack to propagate through the interface between the substrate and the coating and extend beyond the indentation. The high elastic deformation and elastic recovery produced in the substrate, also contribute to the formation of cracks that follows a circular path in external areas to the indentation [50,52]. As indicated in Table 3, these coatings have higher thickness, which suggests an increase of compressive stress. Moreover, the observation of peak shifting in the diffraction patterns (Figure 1b) indicates an increase in the compressive stresses of the coatings with the increase in Ts. The formation of edge cracking is also associated with the decrease in elastic moduli and the increase in H/E and H³/E² ratios [26], as observed in the nanoindentation results (Figure 3). The appearance of edge cracks is further influenced by the reduction in adhesion observed in Table 5 and Figure 4.

3.6. Wear Resistance

Figure 6 shows the coefficient of friction (COF) vs. cycles for D2 steel and the coatings deposited at different Ts, with values in the stabilization stage of 0.95 (substrate), 0.45 (Ts = 200 °C), 0.55 (Ts = 200 °C), and 0.8 (Ts = 200 °C). The coatings showed a lower COF compared to the D2 steel; however, the friction processes differ, particularly in the early stages of the test. For the coatings, during the first 1000 cycles, there is a sudden increase in the COF, indicating a rapid breakdown of asperities. This phenomenon is attributed to the deformation and fracture of microdroplets formed during the cathodic arc deposition process, which exhibit lower energy thresholds for deformation and breakage (see Figure 2). In contrast, the D2 steel undergoes a prolonged stage of asperity breaking, as the contact surfaces between the steel and the pin have lower roughness and deformability, leading to early contact between polished or smooth surfaces. This observation aligns with the roughness values presented in Table 4.

In all materials, the stabilization stage is observed from ~1000 cycles, during which more energy is required for particle breaking. These particles, depending on the material, tend to be harder and more brittle as a result of hardening through plastic deformation. For instance, in the case of the coatings deposited at Ts = 600 °C (with a hardness of ~32 GPa) and Ts = 400 °C (with a hardness of ~30 GPa), the abrasive component of friction is expected to dominate and its stabilization stage exhibits greater instability compared to the coating deposited at lower substrate temperatures. This suggests higher particle generation or wear debris processes. The coatings deposited at Ts = 200 °C exhibit a lower COF, which can be attributed to their lower hardness (around 28 GPa) and lower resistance to plastic deformation. However, the improved mechanical properties of these surfaces compared to D2 steel enable them to withstand the applied loads, resulting in a reduced COF.



Figure 6. Coefficient of friction vs. cycles for the D2 steel substrate and the films deposited at different temperatures.

In Figure 7, SEM images of the wear tracks for the different materials are observed, along with an EDS elemental chemical mapping insert for oxygen. Figure 7a shows the wear track of the D2 steel substrate, where adhesion and ploughing are the dominant wear mechanisms. Highly deformed particles are observed in the center of the track, accompanied by a high concentration of oxygen throughout the wear track. Figure 7b shows the wear track of Ts = $200 \,^{\circ}$ C, revealing signs of micro-scratching and the presence of particles with high deformation in the center of the track. As discussed from the mechanical properties (see Figure 3), this film deposited at the lower temperature showed the lowest hardness and plastic deformation resistance (H^3/E^2), indicating that the debris can deform with lower energy, resulting in reduced abrasiveness during the wear test. This cyclic process of particle deformation, hardening, and breaking, which occurs at a slower rate for this deposition condition, leads to a reduction of the COF as observed in Figure 6. Figure 7c shows the wear track of Ts = $400 \,^{\circ}$ C. Similar to the observations at lower substrate temperatures, deformed particles and micro-scratch grooves are formed in the center of the track. Adhered particles can be seen at the edges of the track, and together with the EDS oxygen analysis, it can be inferred that they consist of oxides of the coating material, as no presence of Fe was observed on the surface. These wear particles, expelled from the track, showed high oxygen content and contribute to increased wear and abrasion on the contact surfaces, which explains the observed increase in COF in Figure 6. Figure 7d shows the wear track of Ts = 600 °C. An increase in abrasion, as well as in the amount of oxygen in the worn surface and the presence of particles in the center and in the corners of the wear track are observed. Despite the detected increase in hardness and plastic deformation resistance for this substrate temperature, the formation of particles intensifies the abrasive component of friction, resulting in an elevated COF (see Figure 6).

The observed wear mechanisms are consistent with the wear rate (k) depicted in Figure 8. The D2 steel substrate shows a high value of k, which is attributed to the ploughing generated by numerous particles adhered to the surface. In contrast, the coatings deposited at different temperatures demonstrate lower wear rates (approximately one order of magnitude lower). However, in alignment with the hardness trend, the wear rate increases with the substrate temperature. This increase in wear rate is associated with the increase in abrasion resulting from the presence of hard particles. These particles undergo a cyclic process of deformation, hardening, and breaking. Eventually, they are expelled from the wear track and accumulate at the edges, exposing the bare surface for the repetition of the wear process. This phenomenon was analyzed in the coatings deposited at Ts of 400 $^{\circ}$ C and 600 $^{\circ}$ C (see Figure 7).



Figure 7. SEM images of the wear track, including the oxygen (O) EDS mapping insert for: (a) AISI D2 steel, (b) Ts = $200 \degree C$, (c) Ts = $400 \degree C$, and (d) Ts = $600 \degree C$.



Figure 8. Wear rate for the D2 steel substrate and the coatings deposited at different temperatures.

In the case of the substrate temperature of $Ts = 200 \degree C$, the aforementioned process took a longer time, and a significant number of particles were observed within the wear track. Although the friction coefficients obtained in this study are higher than those reported in the literature, the wear rate values are approximately one order of magnitude lower [25]. This indicates an improvement in the wear resistance of the material compared to results obtained by other researchers under conditions of severe wear, higher loads, and longer distances.

The tribological behavior of coated surfaces is influenced by various intrinsic and extrinsic factors. Intrinsic factors include parameters associated with film deposition and the counterpair, such as roughness, chemical composition, the relationship between the mechanical properties of the film, substrate, and the counterpair, as well as the stress state at the interface, which directly affects the adhesion of the coating. On the other hand, extrinsic factors include load (and consequently contact stress), speed, type of movement, atmospheric conditions, temperature, and time (or distance or number of cycles) [9,53]. The complexity and dynamic nature of these factors often lead to contradictory trends when evaluating the effect of substrate temperature on the tribological properties of coatings, as they directly influence the intrinsic parameters.

For instance, studies conducted on TiN and WTiN coatings deposited by DC magnetron sputtering have shown that increasing the substrate temperature leads to an increase in both the coefficient of friction (COF) and the wear rate (k). In the case of TiN coatings, this increase is attributed to a reduction in hardness, an increase in the modulus of elasticity, and a decrease in the H/E ratio with increasing Ts. However, no data regarding coating adhesion were reported [54]. On the other hand, for WTiN coatings, the increase in COF is attributed to a reduction in the critical load Lc1 with increasing Ts, but no data on mechanical properties or critical loads Lc2 were provided [55]. It should be noted that the counterparts and contact stresses were similar in both studies. In comparison to these previous research works, the present study observed an increase in hardness, a slight reduction in the average value of E (elastic modulus), and an increase in the average value of H/E (hardness-to-modulus ratio), resulting in a decrease in adhesion.

Furthermore, studies on TaN coatings deposited by magnetron sputtering have reported that increasing Ts leads to a reduction in COF. In this case, the improvement in tribological properties is attributed solely to the change in the crystallographic texture of the material with substrate temperature, without providing data on mechanical properties or material adhesion [56]. On the other hand, coatings such as WC and AlCrWTiMoN did not exhibit changes in COF as a function of increasing substrate temperature, despite reporting an increase in mechanical properties [57,58].

Numerous researchers have investigated the tribological properties of TiN coatings under conditions simulating severe wear encountered in cutting tools. These studies have shown that the friction coefficients of TiN can range from 0.3 to 0.8, depending on the specific contact conditions. Under high loads and moderate speeds (<50 cm/s), the coefficient of friction tends to decrease due to the formation of lubricating oxide layers. However, wear rates significantly increase, exceeding $30 \times 10^{-4} \text{ mm}^3/\text{Nm}$ [59–62]. It has also been observed that dominant wear mechanisms for TiN coatings include abrasion, scratching, and ploughing caused by hard particles. However, most references primarily focus on coatings with low thicknesses (<2 µm), resulting in relatively short lifetimes of less than 2000 cycles. After wear occurs, even partially, both the coefficient of friction and wear rate tend to increase, reaching values as high as 0.9 and 40×10^{-4} mm³/Nm, respectively [59,60,62]. Similarly, studies have demonstrated that incorporating elements that stabilize oxide formation, such as Al in TixAlyN [62,63], Hf in TixHfyN [9], and Nb in TiNbN [25], can lead to reductions in the coefficient of friction and abrasion at both low and high temperatures. These modifications have resulted in an extended useful life for the surface, ultimately enhancing the overall performance of the material in applications including cutting tools, cold and hot forming and drawing, erosion, and impact [63,64].

Therefore, it is necessary to analyze the influence of intrinsic parameters on the wear resistance of coated surfaces on a case-by-case basis. In the case of TiNbN coatings deposited in this study, in contact with Al_2O_3 balls, the tribological response is associated with the increase in mechanical properties and the reduction in adhesion with Ts, leading to the presence of abrasive particles that increase the COF and wear. However, the deposition of these coatings reduces wear on the substrate by an order of magnitude.

4. Conclusions

The tribological properties of TiNbN coatings, deposited using cathodic arc, were investigated under severe wear conditions that simulated cutting environments. The temperature of the substrate was varied during the study. The coatings exhibited friction coefficients ranging from 0.45 to 0.8, and wear rates between 0.08 and 0.23×10^{-4} mm³/Nm were observed. These values were lower than those observed for the AISI D2 steel substrate. Additionally, a quasi-stable friction stage was observed after approximately 1000 cycles. The wear processes observed on the surface of the TiNbN coatings were primarily associated with abrasion mechanisms, particularly involving third-body interactions (scratching and ploughing) and tribo-oxidation. These mechanisms are highly beneficial for cutting tools, as the formation of hard particles enhances material removal capacity, while the formation of stable oxides improves the thermal stability of the tool.

The behavior of the wear particles dominated the tribological response of the surfaces. The surface characteristics were especially influential in the TiNbN coatings deposited by cathodic arc, due to the formation of microparticles and pores, typical of the coatings obtained by this technique.

For the D2 steel substrate, particles adhering to the surface and ploughing were observed, which generated a high friction coefficient and wear. When depositing the TiNbN coatings with different temperatures, a reduction of the wear rate of one order of magnitude was observed. However, by increasing the substrate temperature, particles with brittle behavior and smaller size increased abrasion and wear. This was related to the increase in hardness and plastic deformation resistance and a decrease in adhesion with substrate temperature.

Through EDS elemental chemical mapping, an increase in the oxygen during wear was observed with increasing substrate temperature. While in the D2 steel substrate, oxygen is concentrated inside the wear track, in the coatings an increase was observed at the edges, which was accentuated with the increase in substrate temperature. This is associated with the presence of chemically activated particles, which showed plastic deformation and rupture.

An increase in the substrate temperature reduces both the cohesive load (Lc1) and the adhesive load (Lc2). However, the failure mechanisms found were similar, regardless of temperature, and were related to lateral and conformal cracks for Lc1 and chipping for Lc2.

A similar effect was observed in the cracking patterns generated by micro-indentation, where picture frame cracks were generated within the indentation regardless of the substrate temperature. However, when increasing the temperature, the generation of radial cracks was observed, which propagate through the interface between the substrate and the coating. These types of cracks are associated with deformation of the substrate away from the indentation and the inability of the coating to "accommodate" the plastic conditions and a reduction in adhesion is indicated.

Author Contributions: J.M.G.-C.: Conceptualization, methodology, formal analysis, investigation, resources, data curation, writing—original draft preparation. C.L.M.: investigation, formal analysis, writing—original draft preparation. C.O.-P.: investigation, Conceptualization, validation, writing—review and editing. A.H.-M.: Conceptualization, formal analysis, writing—review and editing, supervision. J.F.P.: Conceptualization, writing—review and editing, project administration, funding acquisition. All authors have read and agreed to the published version of the manuscript.

Funding: The authors would like to thank the Dirección de Investigaciones of the University of Ibagué for the financial support for the development of the project code 19-506-INT. Juan Manuel Gonzalez-Carmona also thanks the Investigadoras e Investigadores por México program (previously Cátedras-CONAHCYT) sponsored by CONAHCYT.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The data presented in this study are available on request from the corresponding author. The data are not publicly available because the results correspond to partial data from a broader investigation financed by CONAHCYT and the University of Ibagué and the information associated with future technological developments will be subject to intellectual property protection.

Conflicts of Interest: The authors declare no conflict of interest.

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Article Low-Temperature Solution-Processed HfZrO Gate Insulator for High-Performance of Flexible LaZnO Thin-Film Transistor

Yeoungjin Chang^{1,2}, Ravindra Naik Bukke^{3,*}, Jinbaek Bae¹ and Jin Jang^{1,*}

- 1 Advanced Display Research Center, Department of Information Display, Kyung Hee University, Seoul 02447, Republic of Korea; yjchang@gachon.ac.kr (Y.C.); jbbae@tft.khu.ac.kr (J.B.)
- 2 Department of Semiconductor Display, Gachon University, Seongnam-si 13120, Republic of Korea
- School of Mechanical & Materials Engineering, Indian Institute of Technology Mandi,
 - Mandi Pradesh 175075, India
- Correspondence: ravindra@iitmandi.ac.in (R.N.B.); jjang@khu.ac.kr (J.J.)

Abstract: Metal-oxide-semiconductor (MOS)-based thin-film transistors (TFTs) are gaining significant attention in the field of flexible electronics due to their desirable electrical properties, such as high field-effect mobility (μ_{FE}), lower I_{OFF}, and excellent stability under bias stress. TFTs have widespread applications, such as printed electronics, flexible displays, smart cards, image sensors, virtual reality (VR) and augmented reality (AR), and the Internet of Things (IoT) devices. In this study, we approach using a low-temperature solution-processed hafnium zirconium oxide (HfZrOx) gate insulator (GI) to improve the performance of lanthanum zinc oxide (LaZnO) TFTs. For the optimization of HfZrO GI, HfZrO films were annealed at 200, 250, and 300 °C. The optimized HfZrO-250 °C GI-based LaZnO TFT shows the μ_{FE} of 19.06 cm²V⁻¹s⁻¹, threshold voltage (V_{TH}) of 1.98 V, hysteresis voltage (V_H) of 0 V, subthreshold swing (SS) of 256 mV/dec, and I_{ON}/I_{OFF} of ~10⁸. The flexible LaZnO TFT with HfZrO-250 °C GI exhibits negligible ΔV_{TH} of 0.25 V under positive-bias-temperature stress (PBTS). The flexible hysteresis-free LaZnO TFTs with HfZrO-250 °C can be widely used for flexible electronics. These enhancements were attributed to the smooth surface morphology and reduced defect density achieved with the HfZrO gate insulator. Therefore, the HfZrO/LaZnO approach holds great promise for next-generation MOS TFTs for flexible electronics.

Keywords: flexible; hafnium zirconium oxide; lanthanum zinc oxide; solution-processed; spray pyrolysis; thin-film transistor

1. Introduction

Metal oxide semiconductors (MOS) are gaining significant interest as channel layers in thin-film transistors (TFTs), particularly for active-matrix light-emitting diode (AMOLED) displays [1-3]. These materials exhibit desirable electrical properties, such as high mobility, near-zero threshold voltage, low off-state current, excellent area uniformity, reliability, and cost-effective mass production. MOS-based TFTs hold the potential to supplant conventional polycrystalline-Si (Poly-Si) or amorphous-Si (a-Si) TFTs across diverse applications. Their appeal lies in offering higher performance characteristics, including improved carrier mobility and lower off-state leakage. Moreover, MOS-based TFTs can be fabricated via cost-effective and scalable processes, making them a viable candidate for next-generation electronic devices. As a result, these TFTs present a compelling alternative for enhancing electronic technologies and fostering innovation in various industries [1–3]. The fabrication of MOS TFTs can be achieved through either solution [1–5] or vacuum process [1,6]. Solution processes [1–5], including spray pyrolysis, spin coating, and inkjet printing, are commonly employed for MOS TFT fabrication [7-19]. Solution processes offer the advantage of operating at low temperatures, facilitating the deposition of metal-oxide-semiconductor (MOS) films on flexible substrates. This characteristic is essential for the development of flexible electronics as it avoids substrate damage and allows for the fabrication of bendable

Citation: Chang, Y.; Bukke, R.N.; Bae, J.; Jang, J. Low-Temperature Solution-Processed HfZrO Gate Insulator for High-Performance of Flexible LaZnO Thin-Film Transistor. Nanomaterials 2023, 13, 2410. https://doi.org/10.3390/ nano13172410

Academic Editors: Jose Maria De Teresa, Ricardo Lopez Anton, Yia-Chung Chang and Sion Federico Olive Méndez

Received: 5 July 2023 Revised: 1 August 2023 Accepted: 16 August 2023 Published: 25 August 2023



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and stretchable devices [1]. In solution-processed oxide TFTs, high-k dielectric materials, for example, aluminum oxide (AlOx) [12,20], hafnium oxide (HfOx) [21], zirconium oxide (ZrOx) [2,10,17,22], aluminum zirconium oxide (AlZrOx) [13,23], boron-doped ZrOx (BZrO) [9], hafnium zirconium oxide (HfZrOx) [24], and lanthanum-doped ZrOx (LaZrO), are employed to achieve high-performance devices. While other MO semiconductors, such as indium gallium tin oxide (IGTO) [25,26] and indium gallium zinc oxide (IGZO) [5] TFTs, typically utilize a SiO₂ gate insulator, solution-processed oxide TFTs offer the advantage of utilizing high-k dielectrics for improved performance [8].

The utilization of high-k gate dielectric materials through solution processes holds tremendous promise in realizing high-performance thin-film transistors (TFTs). These materials offer advantageous electrical properties, such as higher dielectric constants, enabling enhanced control of charge carriers in the transistors. Additionally, the solutionbased approach allows for cost-effective and scalable fabrication, making it a viable option for advancing next-generation electronic devices with improved efficiency and functionality. J. Li et al. report ZTO/AlZrOx TFT with μ_{sat} of 12.5 cm²V⁻¹s⁻¹, V_{TH} of 0.3 V, I_{ON}/I_{OFF} of 8×10^7 , and SS of 0.150 V/dec [27]. Tue et al. demonstrated the use of LaZrO gate dielectric in ZrInZnO TFTs, resulting in a saturated mobility (μ_{sat}) of 6.23 cm²V⁻¹s⁻¹, I_{ON}/I_{OFF} of 10⁹, and SS of 0.19 V/dec [8]. Park et al. report In₂O₃/ZrO₂:B TFT with μ_{sat} of 39.3 cm²V⁻¹s⁻¹, V_{TH} of 2.46 V, I_{ON}/I_{OFF} of 10⁷, and SS of 0.263 V/dec [9]. When considering practical applications, TFTs are fabricated on flexible plastic substrates, such as polyethylene naphthalate (PEN), polyethylene terephthalate (PET), and polyimide (PI). These plastic substrates offer mechanical flexibility, making them ideal candidates for foldable or flexible electronics and displays. Consequently, a low-temperature process becomes essential for compatibility with these substrates. Numerous research groups have focused on developing doped ZrOx gate insulators to enhance the performance of flexible metal oxide TFTs [2,22].

In this study, we present the utilization of a low-temperature solution-processed hafnium zirconium oxide (HfZrOx) GI to achieve high-performance LaZnO TFTs. The HfZrO films were carefully annealed at a temperature of 200, 250, and 300 °C, respectively, for optimization. The optimized HfZrO-250 °C GI-based LaZnO TFT demonstrates an impressive field-effect mobility (μ_{FE}) of 19.06 cm²V⁻¹s⁻¹, a low threshold voltage (V_{TH}) of 1.98 V, and an exceptionally sharp subthreshold swing (SS) of 256 mV/dec. Notably, the device exhibits zero hysteresis voltage (V_H) and an outstanding I_{ON}/I_{OFF} ratio of $\sim 10^8$, ensuring high-performance transistor operation. Furthermore, the flexible HfZrO-250 °C/LaZnO TFT exhibits remarkable stability under positive-bias-temperature stress (PBTS) with minimal ΔV_{TH} , indicating the reliability of the device over the extended operation. These exceptional enhancements can be attributed to the smooth surface morphology achieved by the HfZrO GI and the reduced defects at the interface between the HfZrO gate insulator and the oxide semiconductor (LaZnO). Our findings establish the HfZrO/LaZnO approach as a highly promising avenue for developing flexible oxide TFTs, especially for next-generation flexible displays. The novel combination of materials and the low-temperature solution processing offer significant potential for advancing flexible electronics.

2. Materials and Methods

To prepare the HfZrO precursor solution, we dissolved zirconyl chloride hydrated (ZrOCl·8H₂O) and hafnium chloride (HfCl₄) in a mixture of ethylene glycol (65%) and acetonitrile (35%). The resulting solution, 20 mL in volume, was transferred to a 0.250 L flask. The temperature was steadily increased from room temperature (RT) to 95 °C in 10 °C increments. The solution was maintained at 95 °C for 10 min, resulting in the formation of a transparent precursor solution after cooling to RT. For the synthesis of the 0.2 M LaZnO precursor solution, zinc acetate dihydrate, lanthanum (III) nitrate hexahydrate, and ammonium acetate were added to a solvent called 2-Methoxyenthonal (2ME). The stoichiometry of HZO and LaZnO films are $H_{0.10}Z_{0.90}O$ and $La_{0.10}Z_{0.90}O$, respectively.

The detailed method for preparing the HZO and LaZnO precursor solution can be found elsewhere [2,24]. The precursor solutions were stirred for 2 h under an N2 environment to ensure homogeneity. Finally, a 0.45 μ m polytetrafluoroethylene (PTFE) filter was employed to obtain particle-free precursor solutions.

The HfZrO film was deposited via spin coating onto a glass substrate at room temperature in the ambient environment. After deposition, the sample was placed on a hot plate at 140 °C for 5 min and subsequently annealed in an air furnace at temperatures ranging from 200 to 300 °C. The resulting HfZrO thin films were labeled as HfZrO-200 °C, HfZrO-250 °C, and HfZrO-300 °C, corresponding to the annealing temperatures. The LaZnO film, on the other hand, was deposited using spray pyrolysis onto a glass substrate at a substrate temperature of 350 °C.

In our fabrication process, we employed a bottom gate and top contact configuration for the LaZnO TFTs. Initially, a 40 nm molybdenum (Mo) film was sputtered onto the substrate and patterned to create the gate electrodes. Following the deposition of the HfZrO film, the sample was subjected to a 5 min treatment on a hotplate at 140 °C. The LaZnO solution was then deposited onto the substrate at a temperature of 350 °C using spray pyrolysis. The thickness of the LaZnO films was measured using the Alpha-Step D-500 Stylus Profiler (D-500 Stylus Profiler, KLA Instrument, Hayward, CA, USA). The LaZnO layer was patterned using conventional photolithography to form the active island. Finally, a 40 nm thick Mo layer was sputtered and patterned to create the source/drain (S/D) electrodes.

For the fabrication of flexible LaZnO TFTs, we employed a bottom gate and top contact (BGTC) structure on a polyimide (PI) substrate. Initially, a thin layer of carbon nanotubegraphene oxide (CNT:GO) composite was deposited through spray pyrolysis at 100 °C [3,8]. Subsequently, a 10 μ m thick PI layer was spin-coated onto the CNT:GO layer and annealed for 2 h under a nitrogen (N₂) atmosphere. To provide a gas barrier, a SiNx/SiOx buffer layer with a total thickness of 125 nm (25 nm for each layer) was deposited. The LaZnO channel layer was then deposited at a substrate temperature of 350 °C via spray pyrolysis. The LaZnO active islands were patterned. Finally, a 40 nm molybdenum (Mo) layer was sputtered and patterned to create the source/drain (S/D) contacts. For a detailed fabrication process flow of the LaZnO TFT, refer to the appropriate literature [2,17].

To characterize the HfZrOx films, we conducted UV-visible spectroscopy (transmittance and absorbance) using a Scinco S-4100 instrument. The film thickness was measured with an Alpha step, while the refractive index was determined using ellipsometry. Surface morphology (including RMS roughness) was examined using atomic force microscopy (AFM). Chemical composition and elemental analysis of the metal oxide films were studied through X-ray photoelectron spectroscopy (XPS) with a PHI 5000 Versa Probe, Ulvac-PHI, Chigasaki, Japan) under pressure of 7.5×10^{-5} mTorr.

The electrical properties of TFTs were measured using an Agilent 4156C semiconductor parameter analyzer. The measurements were conducted at room temperature under dark conditions. The V_{TH} was determined by employing the linear extrapolation method on the $(I_{DS})^{1/2}$ vs. V_{GS} plot, using the *x*-axis intercept. The μ_{sat} was obtained from the linear section of the $(I_{DS})^{1/2}$ vs. V_{GS} curve. The SS was determined from the linear region of the log (I_{DS}) vs. V_{GS} fit using Formula (2).

$$I_{DS} = \frac{1}{2} \frac{W}{L} \mu_{sat} C_{ox} \left(V_{GS} - V_{TH} \right)^2, \tag{1}$$

$$SS = \frac{dV_{GS}}{d(\log I_{DS})} \tag{2}$$

where I_{DS} , W/L, μ_{sat} , C_{ox} , V_{TH} , and V_{GS} are the drain current, channel width, channel length, saturation mobility, gate oxide capacitance, threshold voltage, and gate voltage, respectively.

3. Results and Discussion

Figure 1a illustrates the process flow for fabricating the HfZrOx thin film on a glass substrate. Further details can be found in the Materials and Methods Section. In Figure 1b, it is evident that the HfZrOx thin film exhibits transmittances exceeding 90% in the visible region. The optical band gaps of HfZrO-200 °C, HfZrO-250 °C, and HfZrO-300 °C thin films are shown in Figure 1c. For the UV-Vis experiment, the HfZrO_x films were deposited on the glass, where the absorption of a glass substrate can be negligible [2]. The band gap (E_g) of HfZrO-250 °C is 5.85 eV, as can be seen in Figure 1c [2,28–31]. The Eg was extracted using the formula: $\alpha h\nu = A (h\nu - E_g)^{1/n}$, where $h\nu$, n, A, and α are the photon energy, optical transition exponent, a proportionality constant in the absorption process, and absorption coefficient, respectively. The refractive index (R.I.) of $HfZrO_x$ films was measured by ellipsometry. Figure 1d displays the refractive indices (RI) of HfZrO-200 °C, HfZrO-250 °C, and HfZrO-300 °C, with corresponding values of 1.68, 1.79, and 1.83, respectively. The increase in film density is evident from the RI values observed in the visible range. In metal oxide thin film, the composition of the film density can be correlated with RI values. As the annealing temperature increases, the film density of HfZrOx also increases. A lower RI value indicates an increase in film porosity, which subsequently affects both the optical and electrical properties [2,17,28-30].



Figure 1. (a) Schematic representation of $HfZrO_x$ thin film deposited by spin coating. (b) The transmittances of $HfZrO-200 \,^{\circ}C$, $HfZrO-250 \,^{\circ}C$, and $HfZrO-300 \,^{\circ}C$ thin films are higher than 90% in the visible region. (c) The bandgap of $HfZrO-250 \,^{\circ}C$ thin film obtained from the Tauc plot. The inset of (c) shows a photograph of $HfZrO-250 \,^{\circ}C$ thin film placed on the ADRC logo. (d) The refractive index as a function of the photon energy of $HfZrO-200 \,^{\circ}C$, $HfZrO-250 \,^{\circ}C$, and $HfZrO-300 \,^{\circ}C$ thin films.

Figure 2 illustrates the frequency-dependent capacitance of the HfZrO-200 °C, HfZrO-250 °C, and HfZrO-300 °C GIs. The capacitance was measured with a frequency from 20 Hz to 2 MHz. The capacitance values of HfZrO-200 °C, HfZrO-250 °C, and HfZrO-300 °C are 384, 455, and 476 nF/cm², respectively. In the capacitance curve of the HfZrOx film annealed at 200 °C, a decrease in capacitance is observed from around 10 kHz, while the capacitance remains constant up to 300 kHz for HfZrOx-300 °C, with degradation commencing at 300 kHz. This behavior is attributed to the lower defect density present in the HfZrOx film annealed at 200 °C [24]. The inset in Figure 2 depicts the MIM (Mo/HfZrOx/Mo) structure.



Figure 2. Capacitance vs. frequency of HfZrO-200 °C, HfZrO-250 °C, and HfZrO-300 °C gate insulators (GIs) annealed at different temperatures.

Figure 3a–c presents the surface morphology of HfZrO-200 °C, HfZrO-250 °C, and HfZrO-300 °C films. The root-mean-square roughness (R_{RMS}) values for the HfZrO_x films annealed at 200 °C, 250 °C, and 300 °C are determined to be 0.57 nm, 0.36 nm, and 0.29 nm, respectively, with a scanning area of 2 μ m \times 2 μ m. With increasing annealing temperature, the surface roughness decreases, resulting in a smoother surface morphology [20]. The improved smoothness of the HfZrO_x film surface enhances the interface quality with the channel layer. Consequently, the favorable interface between the gate insulator and the channel layer contributes to the enhanced electrical properties of the LaZnO TFT [2,8,12,20,24–26,29,30].



Figure 3. AFM images (Scan size 2 μ m × 2 μ m) of (**a**) HfZrO-200 °C, (**b**) HfZrO-250 °C, and (**c**) HfZrO-300 °C thin films. The R_{RMS} values of 0.57, 0.36, and 0.29 nm indicate smooth surface morphology.

The O1s XPS spectra were analyzed to investigate the chemical composition of the HfZrO films (Figure 4a–c). The O 1s peak was deconvoluted into three sub-peaks centered around ~529.5 eV (metal oxide, M-O), ~530.5 eV (oxygen vacancy, Vo), and ~532 eV (hydroxyl groups, -OH). The percentages of M-O-M, Vo, and -OH in the HfZrOx films annealed at different temperatures (200 °C, 250 °C, and 300 °C) were determined. The M-O-M percentages were found to be 64.75%, 75.39%, and 77.65%, while the Vo ratios were 24.75%, 17.28%, and 15.98%, and the -OH ratios were 10.50%, 7.33%, and 6.37%, respectively [2,15]. The higher M-O-M content indicates a reduction in oxygen-related defects (Vo + -OH), resulting in fewer defects at the interface between the gate insulator and channel layers. This contributes to improved device performance and interface quality [5,10,14,15,27,31–33].



Figure 4. Deconvoluted O1s spectra of (a) HfZrO-200 °C, (b) HfZrO-250 °C, and (c) HfZrO-300 °C thin films. O1s spectra are deconvoluted into three sub-peaks (M-O, Vo, and -OH), where M = metal, Vo = oxygen vacancy, -OH = hydroxyl group.

The electrical properties of LaZnO TFTs with HfZrO (HfZrO-200 °C, HfZrO-250 °C, and HfZrO-300 °C) gate insulators were studied by measuring the I-V (transfer) curves of TFTs. Figure 5a-c depicts the transfer curves of LaZnO TFTs with HfZrO-200 °C, HfZrO-250 °C, and HfZrO-300 °C, illustrating their hysteresis characteristics, with corresponding electrical properties, such as μ_{FF} of (8.49, 19.06, and 22.28) cm²V⁻¹s⁻¹, V_{TH} of (2.60, 1.98, and 1.87) V, V_H of (0.03, 0, and 0) V, and SS of (295, 256, and 231) mV/dec, respectively. The hysteresis curves for the LaZnO TFTs with HfZrO-200 °C, HfZrO-250 °C, and HfZrO-300 °C show the negligible V_{H} , indicating a favorable gate insulator (GI)/channel interface. The reduced number of traps at the GI/channel interface contributes to higher I_{ON} and lower SS, as shown in Figure 5a-c. Achieving a higher M-O-M ratio and minimizing oxygenrelated defects leads to smoother charge transport and reduced charge trapping, resulting in enhanced carrier mobility and stable device operation. With an increase in HfZrO_x annealing temperature, the V_{TH} shifts to a positive V_{GS} due to a decrease in trap states at the interface [2,10,24,33]. The output curves of LaZnO TFTs with HfZrO-200 °C, HfZrO-250 °C, and HfZrO-300 °C are presented in Figure 6a–c, exhibiting clear pinch-off and saturation behavior. The TFTs were tested with V_{DS} sweeping from 0 to +5 V and V_{GS} sweeping from 0 to +5 V (step = 1 V). The absence of current crowding in the low V_{DS} region confirms excellent ohmic contact between the source/drain electrodes and channel layers [5,10,16,29].



Figure 5. (**a**–**c**) The transfer characteristics with hysteresis curves for the LaZnO TFTs with HfZrO-200 °C, HfZrO-250 °C, and HfZrO-300 °C GIs. Hysteresis voltage was obtained at $I_{DS} = 10^{-10}$ A. I_G represents the gate leakage current.

Figure 7a presents an optical photograph of the measurement setup for the flexible LaZnO TFT fabricated on a PI substrate with a HfZrO-250 °C gate insulator (GI). Figure 7b displays the transfer curve of the flexible LaZnO TFT, measured at V_{DS} of 0.1 V by sweeping V_{GS} from -5 to +5 V. The I_{DS}^{1/2} vs. V_{GS} plot with a linear extrapolation line is shown on the right side of the *y*-axis. The flexible LaZnO TFT with HfZrO-250 °C GI exhibits a μ_{FE} of 20.55 cm²V⁻¹s⁻¹, V_{TH} of 1.12 V, and SS of 264 mV/dec. Compared with TFTs on glass substrates, the electrical properties of the flexible LaZnO TFT show almost negligible

changes. To assess the bias stability of the LaZnO TFT with HfZrO-250 °C GI, PBTS was performed on the TFT (at V_{GS} = 5 V for 1 h), as shown in Figure 7c. The evaluation of the transfer curve under PBTS reveals a threshold voltage shift (Δ V_{TH}) of 0.25 V. The positive shift in V_{TH} is attributed to electron trapping at the interface between the HfZrO and LaZnO layers. However, the SS of the LaZnO TFT undergoes a negligible change after 1 h of bias stress, indicating fewer interfacial traps. A higher M-O-M ratio and reduced oxygen-related defects significantly enhance mobility and excellent bias stability of the metal oxide TFT. Thus, the interface quality between HfZrOx and LaZnO plays a crucial role in improving the electrical properties of the TFT.



Figure 6. (a–c) The output curves of LaZnO TFTs with HfZrO-200 °C, HfZrO-250 °C, and HfZrO-300 °C GIs. The channel width and length of the LaZnO TFT used for the measurement are 20 and 10 μ m, respectively.



Figure 7. (a) Photograph of the measurement setup of LaZnO TFT with HfZrO-250 °C gate insulator fabricated on a PI substrate. (b) The transfer curve of the LaZnO TFT measured at the drain voltage $V_{DS} = 0.1$ V by sweeping V_{CS} from -5 to +5 V. (c) Transfer curve of the LaZnO TFT under PBTS for 1 h at 60 °C.

To validate the accuracy of the performances of HfZrO-250 °C/LaZnO TFTs, we fabricated the TFTs in four different runs to ensure precise and reliable data collection. The m_{FE}, V_{ON}, and SS values of the HfZrO-250 °C/LaZnO TFT for Run-I, Run-II, Run-III, and Run-IV are $(17.50 \pm 2.20, 16.95 \pm 2.85, 18.99 \pm 2.15, \text{ and } 18.50 \pm 1.98) \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, $(-1.62 \pm 0.18, -1.56 \pm 0.14, -1.72 \pm 0.21, \text{ and } -1.69 \pm 0.23)$ V, $(253 \pm 13.22, 264 \pm 11.94, 249 \pm 10.89, \text{ and } 261 \pm 8.58)$ mV/dec, respectively, as shown in Figure 8a–c. The small deviation in these values indicates the high reliability and consistency of the fabrication process. The narrow range of fluctuations highlights the robustness of the HfZrO-250 °C/LaZnO TFT performance across multiple runs, reaffirming its potential for practical applications in electronic devices. The HZO film deposited at 350 °C is prone to crystallization and can be a ferroelectric material [33]. As a result, we used spin-coating for the HZO film at 250 °C, which provides a more favorable gate insulator for the LaZnO TFT. The electrical properties of the

solution-processed ZnO-based TFTs with various solution-processed gate dielectrics are reported in the literature, as shown in Table 1 [34–39]. H. Liu et al., demonstrate hysteresis-free Indium gallium zinc oxide (IGZO) TFT with HfOx gate insulator (GI), which exhibits excellent performance characteristics, including a high mobility of 30 cm²V⁻¹s⁻¹, an SS of 68 mV/dec, and a high I_{ON}/I_{OFF} of 10⁶ [40]. In the present work, our HfZrO/LaZnO TFTs display superior performance with high mobility, low subthreshold swing, and a high I_{ON}/I_{OFF} ratio. Furthermore, we successfully fabricated flexible LaZnO TFTs with HfZrO-250 °C GI, which exhibited hysteresis-free behavior, leading to improved electronic device performance and enhanced stability for a wide range of applications [34–36,41].



Figure 8. (a) Mobility (b) V_{ON}, and (c) SS of HfZrO-250 °C/LaZnO TFT as a function of run (Run-I, Run-II, Run-III, and Run-IV). All the TFTs were measured at room temperature in the dark.

Table 1. Comparison of the electrical properties of the solution-processed ZnO-based TFTs with various solution-processed gate dielectrics reported in the literature.

Active/GI	TFT W/L [μm/μm]	Mobility [cm ² V ⁻¹ s ⁻¹]	SS [mV/dec]	Stability (ΔV _{TH} , [V])	Ref.
^(a) LaZnO/ ^(b) ZrO _x	50/10	8.31	218	PBTS (0.10)	[2]
^(b) ZnO/ ^(b) AlO _x	60/10	6.05	550	-	[34]
^(a) ZnO/ ^(a) AlTiO _x	2000/20	10.00	550	-	[35]
^(a) ZnO/ ^(a) HfO _x	2000/20	42.00	-	-	[36]
^(b) ZnO/ ^(b) LaZrO _x	50/10	11.58	249	PBS (0.20)	[37]
^(b) ZnO/ ^(b) SiO ₂	1000/50	3.20	600	-	[38]
^(a) ZnO/ ^(b) ZrO _x	50/10	12.76	260	PBS (0.01)	[39]
^(a) LaZnO/ ^(b) HfZrO	50/10	19.06	256	PBTS (0.23)	[This work]

^(a) Spray Pyrolysis; ^(b) Spin Coating.

4. Conclusions

In summary, this study investigates the use of a low-temperature solution-processed HfZrOx gate insulator (GI) to improve the performance of LaZnO thin-film transistors (TFTs) for potential applications in next-generation flexible displays. To optimize the HfZrO GI, annealing was performed at 200, 250, or 300 °C. The LaZnO TFT with HfZrO-250 °C GI exhibits a μ_{FE} of 19.06 cm²V⁻¹s⁻¹, V_{TH} of 1.98 V, hysteresis voltage (V_H) of 0 V, SS of 256 mV/dec, and I_{ON}/I_{OFF} ratio of ~10⁸. The decrease in hysteresis voltage is critical as it helps to ensure the stability and reliability of the TFT operation. Additionally, the steep subthreshold slope (SS) of 256 mV/dec indicates a sharp turn-on behavior, which is essential for achieving efficient switching. Moreover, the on/off current ratio (I_{ON}/I_{OFF}) of ~10⁸ highlights the ability of the transistor to efficiently control the flow of currents. Under PBTS, the HfZrO-250 °C/LaZnO TFT experiences a threshold voltage shift (ΔV_{TH}) of 0.23 V. These enhancements can be attributed to the smooth surface morphology and reduced defects in the HfZrO gate insulator. Therefore, these findings significantly advance our understanding of the underlying phenomena and pave the way for the development of flexible metal-oxide-semiconductor TFTs for future-generation flexible displays.
Author Contributions: Conceptualization, R.N.B.; Y.C. and J.J.; methodology, Y.C. and R.N.B.; formal analysis, R.N.B. and Y.C.; investigation, R.N.B. and Y.C.; resources, R.N.B. and J.J.; data curation, Y.C.; J.B.; R.N.B. and J.J.; writing—original draft preparation, R.N.B. and Y.C.; writing—review and editing, R.N.B. and J.J.; supervision, J.J.; funding acquisition, J.J. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by the Industrial Strategic Technology Development Program (20010082) funded by the MOTIE, Korea.

Data Availability Statement: We can provide the data if asked.

Conflicts of Interest: The authors declare no conflict of interest.

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Article Magnetism and Thermal Transport of Exchange-Spring-Coupled La_{2/3}Sr_{1/3}MnO₃/La₂MnCoO₆ Superlattices with Perpendicular Magnetic Anisotropy

Vitaly Bruchmann-Bamberg ¹, Isabell Weimer ¹, Vladimir Roddatis ², Ulrich Ross ³, Leonard Schüler ¹, Karen P. Stroh ¹ and Vasily Moshnyaga ^{1,*}

- ¹ Erstes Physikalisches Institut, Georg-August-University Göttingen, Friedrich-Hund-Platz 1,
- 37077 Göttingen, Germany; isabell.weimer@uni-goettingen.de (I.W.); leonard.schueler@uni-goettingen.de (L.S.)
 Helmholtz Centre Potsdam, GFZ German Research Centre for Geosciences, Telegrafenberg,
- 14473 Potsdam, Germany; vladimir.roddatis@gfz-potsdam.de
 IV. Physikalisches Institut, Georg-August-University Göttingen, Friedrich-Hund-Platz 1,
- 37077 Göttingen, Germany; uross@gwdg.de
- Correspondence: vmosnea@gwdg.de

Abstract: Superlattices (SLs) comprising layers of a soft ferromagnetic metal La_{2/3}Sr_{1/3}MnO₃ (LSMO) with in-plane (IP) magnetic easy axis and a hard ferromagnetic insulator La₂MnCoO₆ (LMCO, out-of-plane anisotropy) were grown on SrTiO₃ (100)(STO) substrates by a metalorganic aerosol deposition technique. Exchange spring magnetic (ESM) behavior between LSMO and LMCO, manifested by a spin reorientation transition of the LSMO layers towards perpendicular magnetic anisotropy below $T_{SR} = 260$ K, was observed. Further, 3 ω measurements of the [(LMCO)₉/(LSMO)₉]₁₁/STO(100) superlattices revealed extremely low values of the cross-plane thermal conductivity κ (300 K) = 0.32 Wm⁻¹K⁻¹. Additionally, the thermal conductivity shows a peculiar dependence on the applied IP magnetic field, either decreasing or increasing in accordance with the magnetic disorder induced by ESM. Furthermore, both positive and negative magnetoresistance were observed in the SL in the respective temperature regions due to the formation of 90°-Néel domain walls within the ESM, when applying IP magnetic fields. The results are discussed in the framework of electronic contribution to thermal conductivity originating from the LSMO layers.

Keywords: superlattices; high-resolution STEM; exchange spring magnet; perpendicular magnetic anisotropy; magneto-thermal conductivity

1. Introduction

Mixed valence perovskite manganites with general chemical formula $A_{1-x}A'_xMnO_3$ and double perovskites $A_2BB'O_6$ (here, A = La, Sr; B = Mn, Co) belong to the family of strongly correlated transition metal oxides. Their hallmark is a strong coupling between charge, spin, and lattice degrees of freedom, which results in super- and double-exchange (SE and DE) mechanisms of orbital interactions [1,2]. The variety of magnetic ordering, i.e., para-(PM), ferro-(FM), and anti-ferromagnetic (AFM) accompanied by metal-insulator and/or charge ordering transitions, can be effectively influenced via bandwidth or bandfilling controls, i.e., by means of chemical pressure or hole doping. Moreover, the external control parameters, like temperature, hydrostatic pressure as well as applied magnetic and electric fields were found to strongly influence the phase transitions [3]. A unique field-induced phenomenon found in this material class is colossal magnetoresistance (CMR) or a magnetic field-induced insulator-metal transition [1,4,5]. Perovskite manganites have drawn great and continuous interest for basic and applied research in spintronics, multiferroics, catalysis, optoelectronics, and thermoelectricity [6–10].

Combining materials in superlattices (SL) has proven to be a fruitful pathway in the search for advanced functionality, leading to the discovery of a wide range of novel

Citation: Bruchmann-Bamberg, V.; Weimer, I.; Roddatis, V.; Ross, U.; Schüler, L.; Stroh, K.P.; Moshnyaga, V. Magnetism and Thermal Transport of Exchange-Spring-Coupled La_{2/3}Sr_{1/3}MnO₃/La₂MnCoO₆ Superlattices with Perpendicular Magnetic Anisotropy. *Nanomaterials* 2023, 13, 2897. https://doi.org/ 10.3390/nano13212897

Academic Editors: Jose Maria De Teresa, Ricardo Lopez Anton and Sion Federico Olive Méndez

Received: 29 September 2023 Revised: 30 October 2023 Accepted: 31 October 2023 Published: 3 November 2023



Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). material properties not akin to the parent systems [11–13]. Magnetic SLs exhibit remarkable phenomena such as giant magnetoresistance (GMR) or tunnel magnetoresistance (TMR) and are nowadays widely used in sensing and information storage technologies. Perpendicular magnetic anisotropy (PMA) plays a crucial role in the increase of storage density in hard drives [14,15]. To achieve PMA in manganites, like LSMO, orbital and strain engineering approaches via the choice of appropriate substrates [16], buffer layers [17], or interfaces [18] have been suggested. These strategies are based on the promotion of a preferred occupation of the 3z²-r² orbital, which favors PMA through spin-orbit coupling [19].

Another possibility to realize PMA in a soft FM with in-plane (IP) magnetic anisotropy is a direct-exchange coupling to a hard FM-possessing PMA [20]. Generally, exchangecoupled heterostructures or SLs of hard and soft FMs form the magnetic exchange spring (ESM) [21–25], which enables a gradual rotation or torsion of magnetic moments within the soft FM layers under applied small/moderate magnetic fields. The magnetic moments of the hard FM remain unchanged, thereby creating a spring-like reversible twist of the soft magnetic moments. This phenomenon occurs as long as the applied fields do not exceed the coercive field of the hard FM, ensuring its remanence. The interface spins of the soft FM remain effectively pinned by exchange coupling to the hard layers form a magnetic spring with a spin structure that resembles a domain wall [26,27]. It was shown that magnetoresistance (MR) can originate from the field-induced domain-wall-like twisted spin disorder in ESM NiFe/CoSm bilayers [26], and it was also found in intrinsic domain walls in LSMO nanowires [28].

However, knowledge of the electronic and thermal properties of ESM-coupled layers in manganite-based SLs is scarce [18]. Moreover, to the best of our knowledge, the thermal conductivity of ESM-coupled SLs and the influence of magnetic fields on it have not been studied. In general, thermal conductivity in isolating crystals is mainly based on phononic heat transport, which is affected by crystal symmetry, impurities, and other structural defects or distortions. The additional contribution of free-charge carriers to thermal conductivity in metals and highly doped semiconductors can be calculated using the Wiedemann-Franz (WF) law $\kappa_{\rm el} = \sigma_{\rm el} \times L \times T$ [29], with electrical conductivity $\sigma_{\rm el}$, temperature T, and the Lorenz number $L = \pi^2/3(k_B/e)^2 = 2.45 \times 10^{-8} \Omega \text{ W/K}^2$. However, in non-degenerate semiconductors as well as in strongly correlated or otherwise complex systems, the Lorenz number is not constant and can vary with temperature [30]. This makes the precise disentanglement of lattice and electronic contributions to thermal transport challenging. Still, the change of thermal conductivity in an external magnetic field, dubbed as "magneto-thermal conductivity" [31] and denoted as $MTC = [\kappa(B \neq 0) - \kappa(B = 0)]/\kappa(B = 0)$, can be observed in magnetoresistive materials due to the variation of their electrical conductivity dependent on a magnetic field [32-37].

Here we report an ESM coupling between LSMO and LMCO within $[(LMCO)_n/(LSMO)_n]_m$ SLs epitaxially grown on STO(100) substrates via a metalorganic aerosol deposition (MAD) technique (see Methods section for details). Such an exchange spring with PMA, dictated by the hard magnetic LMCO layers, strongly impacts the electrical and thermal transport properties of SLs through magnetic field control of spin order/disorder. The results obtained highlight an attractive opportunity to study the spin-dependent scattering of charge carriers at domain-wall-hosting interfaces as well as to control the electromagnetic and thermal properties of SLs with a magnetic field.

2. Materials and Methods

2.1. Sample Preparation and Characterization

All oxide film samples were prepared by means of the metalorganic aerosol deposition (MAD) technique. Aerosols of the metalorganic precursor solution (acetylacetonates of the desired metals solved in N,N-dimethylformamide) have been sprayed through compressed air on a heated substrate. By using precise dosing units for liquid precursors as well as in situ growth control by means of optical ellipsometry [38], the single oxide films and heterostructures can be grown with monolayer accuracy. The substrate temperatures for

growth of the crystalline oxide films were $T_{dep,cryst} = 900-950$ °C and the deposition rate was $v_{dep} = 0.1$ nm/s. For amorphous growth, a temperature of $T_{dep,amorph} = 360$ °C with a deposition rate of $v_{dep} = 0.05$ nm/s was used. The STO substrates (Crystal GmbH, $10 \times 5 \times 0.5$ mm³) were TiO₂ terminated based on an etching procedure [39] using an ammonium fluoride buffered hydrofluoric acid etchant and tempering for 1 h at T = 965 °C in the air to obtain a flat terrace morphology. The [(LMCO)_n/(LSMO)_n]_m/STO(100) SLs were grown with an overall thickness of around d ≈ 75 nm by varying the superlattice repetition number "m".

Four-probe electrical conductivity and magnetization measurements were carried out by Quantum Design GmbH (Darmstadt, Germany) PPMS and SQUID magnetometers MPMS XL and MPMS 3. The latter has been used for the rotator measurements (Standard rotator sample holder with $\alpha = 0^{\circ}$ corresponding to the in-plane direction ($\alpha = 90^{\circ}$ out-ofplane), samples were cut to 3 × 3 mm² to fit the holder).

The heater (150 nm thick Au layer grown on 5 nm thick Cr adhesion layer) for thermal conductivity measurements by the 3 ω method was deposited by thermal evaporation (Cr) and magnetron sputtering (Au) followed by structuring with an optical lithography lift-off (Karl SUSS MJB4 (SÜSS MicroTec, Garching bei München, Germany) exposure unit, Allresist AR-P 5350 photoresist (Micro Materials Pty Ltd., Malvern Victoria, Australia). The dimensions of the heater line (width 2b = 25 μ m, the length between the voltage leads 1 \approx 1 mm) were measured by optical microscopy and additionally confirmed by scanning electron microscopy. To electrically decouple the metal heater from the analyzed and potentially conductive samples, insulating capping layers of amorphous alumina (am-Al₂O₃) were used.

X-ray measurements were conducted with the Bruker Advance D8 (Ettlingen, Germany) diffractometer. X-ray reflectivity (XRR) was used to obtain the film thicknesses as well as the density of amorphous am-Al₂O₃ capping layers $\rho_{am-Al_2O3} = 3.3(2)$ g·cm⁻³ from single film measurements after fitting with the *GenX* program [40].

Scanning Transmission Electron Microscopy (STEM) was performed using a Thermo Fisher Scientific (TFS) (Thermo Fisher Scientific, Waltham, MA, USA) Themis Z 80-300 (S)TEM operated at 300 kV, equipped with a TFS SuperX Energy Dispersive X-ray (EDX) detector and a Gatan Imaging Filter (GIF) Continuum 1065. The microscope was tuned for a sub-Angstrom resolution with a beam convergence angle of 21.4 mrad. Specimens for STEM were prepared with a lift-out Focused Ion Beam technique using a TFS Helios G4UC dual-beam instrument. The octahedral tilt within the Mn-O layers was measured from iDPC-STEM images using the Atomap library for Python [41], by fitting 2D Gaussians to individual atom contrast features and evaluating the collection of atom positions regarding the tilt of the Mn-O bonds within the zone axis projection.

2.2. Measurements of Thermal Conductivity by the 3ω Method

The 3 ω method is a well-established technique for measuring thermal conductivity, especially of thin films [42]. The home-built setup used here was built based on the original setup by Cahill. A metal stripe on top of the sample acts both as a heater and a thermometer. Sourcing AC (here using the Keithley 6221 (Tektronix UK Ltd., Berkshire, UK) current source) provides Joule heating of the metal line such that its temperature oscillates at a doubled frequency. Detecting the temperature oscillation via the calibrated temperature-dependent electrical resistance oscillation of the heater element is achieved by measuring the 3rd harmonic (3 ω) AC voltage by lock-in amplification (here by Stanford Research Systems SR830, Sunnyvale, CA, USA). To suppress the dominant ohmic voltage drop, an in-situ hardware subtraction of a reference resistor with a low-temperature coefficient of resistance (Vishay Z201 foil resistor, Vishay Electronic GmbH, Selb, Germany) is realized by a voltage divider and instrumentation amplifiers (Texas Instruments INA103, Freising, Germany). The measured in-phase and out-of-phase 3 ω voltage oscillations are then used to calculate the complex temperature oscillation of the metal heater.

The 3 ω measurements have been carried out using the PPMS cryostat for temperature control. Continuous measurements of temperature-dependent temperature oscillations were performed at a cooling rate of 1 K/s with 3 s lock-in integration time at excitation angular frequencies of ln(ω) = 5.5 and 6, respectively.

Using an analytical expression for frequency-dependent temperature oscillation of a metal heater/thin film/substrate system derived by Borca-Tasciuc et al. [43], which was subsequently improved by the Olson, Graham, and Chen's thermal impedance model [44], allows for fitting the data to obtain both thermal diffusivity and thermal conductivity of the substrate as well as the thermal resistance of a film on the substrate. Additional statistical evaluation for an estimation of the noise level of the raw 3-omega (voltage) signal has been also performed. Converting the signal to the temperature oscillation and subsequently calculating thermal resistance within the standard 3-omega evaluation procedure, results in an uncertainty of the thermal resistance of $\sigma(R, \text{thermal}) = 2 \times 10^{-10} \text{ m}^2\text{K/W}$. Using the LSMO sample as an example, the error propagation leads to a statistical random error for thermal conductivity of $\sigma(\text{kappa}) = 0.02 \text{ Wm}^{-1}\text{K}^{-1}$, which corresponds to a 2-sigma limit of ~2%.

3. Results and Discussion

3.1. Structure and Microstructure of LSMO/LMCO Superlattices

The SL samples composed of LMCO and LSMO, i.e., $[(LMCO)_n/(LSMO)_n]_m/STO(100)$, with layer thicknesses ranging from n = 1-24 unit cells (u.c.), were grown with SL repetition numbers m between 4 and 96 to ensure an overall thickness of d \approx 75 nm for all samples. The structure and microstructure of the representative SLs with n = 9, 24 u.c. and m = 11, 4are shown in Figure 1. The HAADF-STEM images reveal an epitaxial growth of LSMO and LMCO layers with regular repetition of the layers, each showing thicknesses close to the nominal ones. Moreover, the interfaces look sharp and flat in good agreement with the root-mean-square roughness of $S_q \approx 0.2$ nm for the n = 9 u.c. SL and $S_q \approx 0.5$ nm for the n = 24 u.c. SL, determined at the SL surfaces by means of atomic force microscopy (Figure S1, in Supplemental Material (SM). The small angle X-ray reflection (XRR) (see Figure S2 in SM) additionally confirms the thickness of individual layers to be close to the nominal values. Finally, X-ray diffraction (XRD) patterns evidence an out-of-plane epitaxy with c-axis lattice parameters within the range of $c \approx 0.3849$ –0.3855 nm for both LMCO and LSMO layers (see Figure S2, SM) This is not very surprising given the similarity in pseudocubic bulk lattice parameters of LMCO and LSMO, both having values close to $c \approx 0.388$ nm [45,46] and sharing the same tensile stress state induced by the STO(100) substrate as well. One has to point out weak HAADF-STEM contrast between the LMCO and LSMO layers, having slightly differing composition at A-sites $(La/La_{0.7}Sr_{0.3})$ as well as very similar atomic masses of B-site cations, i.e., Co(59) and Mn(54). This makes the analysis of interfacial sharpness and intermixing at the atomic scale difficult. The additionally performed TEM chemical analysis of the [(LMCO)₉/(LSMO)₉]₁₁/STO(100) SL by using energy dispersive X-ray microanalysis (EDX) (see Figure S3, SM) has revealed a clear chemical contrast between LMCO and LSMO as well as detected Co/Mn intermixing at the interfaces with a thickness ~2 u.c. This is in line with XRR results.

3.2. Magnetic Exchange Spring in LSMO/LMCO Superlattices

In order to elaborate on the magnetic properties of $[(LMCO)_n/(LSMO)_n]_m/STO(100)$ SLs, we first introduce single films of LSMO/STO(100) and LMCO/STO(100). The optimally doped perovskite manganite La_{0.7}Sr_{0.3}MnO₃ (LSMO) is a well-known soft FM metal with an in-plane (IP) magnetic easy axis and magnetotransport properties governed by the DE interaction [47]. An almost 100% spin polarization at the Fermi level in the ground state [48] makes LSMO promising for spintronic applications. In Figure 2a, field-cooled IP and out-of-plane (OOP) magnetization measurements of a MAD-grown LSMO/STO(100) thin film with a thickness of d = 25 nm are shown, exhibiting a Curie temperature of $T_{C,LSMO}$ = 355 K. Together with the rotator measurements of the remanent magnetization



Figure 1. High angular annular dark field (HAADF) scanning transmission electron microscopy (STEM) images of the representative [(LMCO)₂₄/(LSMO)₂₄]₄/STO(100) (**left**) and [(LMCO)₉/(LSMO)₉]₁₁/STO(100) (**right**) SLs.

(Figure 2b) and measurements of magnetic hysteresis (Figure S4, SM), we conclude a soft FM behavior with an IP easy axis and a small coercive field $\mu_0 H_c(5 \text{ K}) \approx 3 \text{ mT}$ in agreement

The double perovskite La₂MnCoO₆ (LMCO) is an insulating hard FM characterized by an SE mechanism [45]. A MAD-grown LMCO/STO(100) film of d = 40 nm displays a high $T_{\rm C}$ = 225 K (Figure 2c) and possesses a large coercive field of $\mu_0 H_c(5 \text{ K}) \approx 1.1 \text{ T}$ (see Figure S3, SM). These values, being comparable to those measured in the B-site ordered bulk material [45] and previously studied MAD-grown LMCO thin films [50,51], evidence a right cation stoichiometry and an absence of oxygen deficiency, which is known to suppress magnetism in rf-sputtered LMCO films [52]. In addition, our LMCO/STO(100) film possesses an OOP magnetic easy axis as verified by the angle-dependent measurements of remanent magnetization shown in Figure 2d. This observation agrees well with previous reports on LMCO/STO(100) films [53,54]. Small deviations of the easy axes from the pure IP or OOP orientations in the presented measurements can either be explained by the competition between the crystal (OOP) and shape (thin film, IP) anisotropies or, most probably, they originate from an error of angle settings (here typically $\pm 5^\circ$).

Figure 3a presents measurements of the IP magnetic moment of selected SLs, revealing an unusual magnetic behavior. Namely, the SLs with n = 9–24 u.c. show a spin reorientation (SR) transition at $T_{SR} \approx 260$ K, at which the magnetic easy axis gradually changes towards PMA at low temperatures as evidenced by the temperature-dependent angle-resolved measurements of remanent magnetization, shown in Figure 3b representatively for the SL with n = 9 u.c. SLs with very thin layers n = 1–6 u.c. (see Figure S5, SM) do not reveal the SR transition, which is probably caused by two reasons: (1) very thin LSMO layers become "magnetically dead", implying a significant reduction of $T_{C,LSMO} < 200$ K when the LSMO thickness is reduced down to few unit cells [55–57] and (2) the Co/Mn intermixing (see Figure S3, SM) in very thin layers n = 1–3 u.c. leads to the formation of a mixed (La,Sr)(Co,Mn)O₃ with an unknown composition.

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Figure 2. Normalized field-cooled IP and OOP magnetization of (a) LMCO/STO(100) and (c) LSMO/STO(100) single films with thickness d = 25 nm and 40 nm, respectively. The respective polar plots (**b**,**d**) show the angle-resolved measurements of the normalized remanent magnetization. The arrows indicate the position of the easy axis.

A similar magnetic PMA spin reorientation has been reported in heterostructures of perovskite LSMO and brown-millerite LaCoO_{2.5} (B-LCO), i.e., $[(LSMO)_i/(B-LCO)_j]_m/STO(100)$ heterostructures, by Zhang et al. [18]. They interpreted the SR based on the symmetrymismatch-driven perovskite/brown-millerite interfacial elongation of the oxygen octahedra, which implies an orbital reconstruction of the Mn ions within the interfacial LSMO. Such reconstruction was suggested to change the magnetic easy axis of LSMO towards a PMA geometry. The magnetic contribution of the B-LCO was neglected due to the very low Curie temperature of a single B-LCO/STO(100) film, $T_{C,B-LCO} << T_{SR}$. Thus, they attributed the PMA observed in their SLs to the structural and orbital reconstruction, induced by the symmetry breaking at the perovskite/brown-millerite interface.

We have carried out measurements of both IP and OOP field-cooled magnetization under various external magnetic fields (Figure 4) on the SL with n = 9 u.c., which has the highest interface density among the samples that exhibit the SR transition. A similar behavior to that reported by Zhang et al. [18] has been observed, i.e., (1) IP spin reorientation for T < T_{SR} \approx 260 K; (2) saturation of the OOP magnetization at low temperatures for cooling fields $B \ge 0.2$ T; and (3) an IP-OOP crossover at lower fields and temperatures around 260 K. Note, that in contrast to Zhang et al. [18], our [(LMCO)_n/(LSMO)_n]_m/STO(100) SLs possess a perovskite/perovskite heteroepitaxy without any structural symmetry mismatch at the interface as evidenced by high-resolution HAADF-STEM and iDPC-TEM measurements



(see Figure S6 in SM). Evidently, the interfaces appear coherent and show no visible abrupt changes in the octahedral tilt/rotation angles.

Figure 3. (a) Field-cooled IP magnetic moment component of $[(LMCO)_n/(LSMO)_n]_m/STO(100)$ SLs with different layer thicknesses n = 6, 9, 12 and 24 u.c. and bilayer numbers m = 16, 11, 8, 4, respectively. The arrows mark the temperatures used for the rotator measurements of normalized remanence of the n = 9 u.c. $[(LMCO)_9/(LSMO)_9]_{11}/STO(100)$ SL (b), showing a change of magnetic anisotropy from an OOP to an IP direction around 250 K upon warming from 5 K to 280 K. Here the arrows indicate the apparent position of the easy axis.



Figure 4. IP and OOP field-cooled magnetization measurements of the n = 9 u.c. [(LMCO)₉/(LSMO)₉]₁₁/STO(100) SL in different magnetic fields.

According to our magnetization measurements, the observed spin reorientation in our SLs can more likely be explained by the interplay of different magnetic easy axes and strongly different coercive fields of LMCO and LSMO, leading to the formation of a "magnetic exchange spring" (ESM)-coupled heterostructure. The reduction of the IP magnetization of our SLs below T_{SR} would then be attributed to the OOP rotation of magnetic moments within the LSMO due to the exchange coupling to the hard magnetic LMCO with PMA. This would indeed require a slightly increased T_C of either the LMCO layer itself or, at minimum, its interfacial region near the layer LSMO, up to a value of $T_{\text{C,SL-LMCO}} \approx T_{\text{SR}} \approx 260 \text{ K}$ within the SLs. An independent method for estimating the T_{C} of LMCO layers in SLs is provided by Raman spectroscopy measurements, which allow for measuring the spin-spin correlation induced anomalous shift of Raman lines in FM manganites due to spin-phonon coupling [58]. As one can see in Figure S7 (SM), the anomalous downshift of the dominating LMCO Raman line around 600 cm⁻¹, induced by the FM transition, indeed starts at $T_{\text{C}} \approx 260 \text{ K}$, which is significantly larger than the $T_{\text{C}} = 225 \text{ K}$ of single LMCO films determined also by Raman spectroscopy [50]. Thus, thin (9–24 u.c.) LMCO layers in LMCO/LSMO SLs do have an enhanced T_{C} compared to single LMCO/STO films likely because of the reduced dimensionality and optimal interfacing with FM metallic LSMO layers.

Due to the orthogonality of the easy axes of the LSMO and LMCO layers, the formation of 90° Néel-type domain walls at the interfaces between the layers at low temperatures is favored. Such ESM made from the insulating LMCO and metallic/magnetoresistive LSMO counterparts should certainly give rise to a unique field-dependent electrical resistivity behavior. Temperature- and field-dependent electrical resistance measurements (current IP, field-cooled) of the n = 9 u.c. SL are shown in Figure 5.



Figure 5. Field-cooled electrical resistance vs. temperature of the [(LMCO)₉/(LSMO)₉]₁₁/STO(100) SL with both current and field applied in-plane. The inset shows the region with positive magnetoresistance.

One can see a metal-insulator transition with a peak temperature around $T_{\rm MI} \approx 320$ K for B = 0 T and a maximal value of CMR(300 K) = -36%. This can be attributed solely to the LSMO, as current flow takes place only within the metallic LSMO. A similar R(T) behavior is known for single LSMO/STO(100) films of comparable thickness and is reported elsewhere [59]. Below T < 250 K, especially in the region around $T \approx 220$ K, the resistance of the SL shows an increase with the magnetic field and magnetoresistance becomes positive MR(220K, B = 1 T) = +4.5% for 0 < B < 5 T (see inset in Figure 5). This is in clear contradiction with the well-known negative CMR effect. Note, that at $T_{\rm SR} = 260$ K, the spin reorientation and the ESM formation set in, resulting in the field-induced spin disorder within the emergent Néel domain-wall, which is expected to increase the electron-spin scattering and thus the resistance of the LSMO. When nearly saturated ($B \ge 5$ T), the spin disorder vanishes as all spins are oriented IP, and the LSMO within the SL again follows its intrinsic negative CMR behavior.

Further, a strong decrease of the resistance below $T \approx 275$ K as well as the apparent stochastic resistance jumps below T < 100-150 K can be seen in Figure 5. The former can be caused by the mutual ferromagnetic proximity, as the magnetic moment of the adjacent LMCO is also the source of an additional magnetic field and thereby able to

cause a reduction of LSMO resistance due to CMR. The other aspect of resistance jumps at lower temperatures might be ascribed to domain-wall pinning and movement as well as creation or annihilation of magnetic domain wall boundaries within the ultrathin LSMO in field-cooled measurements, which is known to alter the resistance of nanoscale LSMO [28]. Upon warming, however, the resistance does not show any jumps, most likely indicating domain rotation rather than domain wall movement (see Figure S8, SM).

The observations mentioned above allow us to model the typical profile of a magnetic exchange spring within the LMCO/LSMO SL as sketched in Figure 6. At temperatures $T_{C,LMCO} < T < T_{C,LSMO}$, the magnetic moments of the LSMO layers lie along their respective IP easy axis direction (Figure 6a). As the temperature falls below $T < T_{C,LMCO}$ and the LMCO becomes OOP ferromagnetic, the exchange coupling at the interface forces the LSMO to rotate OOP, thus favoring Néel-type domain walls at the interfaces (Figure 6b). By increasing the IP magnetic field, the magnetic moments of the LSMO reorient back to the IP direction (d), followed by saturation of the entire SL when the applied magnetic field exceeds the coercive field of the LMCO (e).



Figure 6. Schematic illustrations of the temperature- and magnetic field-dependent magnetic profile within an ESM in $[(LMCO)_n/(LSMO)_n]_m/STO(100)$ SLs: (**a**) $T_{SR} < T < T_{C, LSMO}$ (**b**) PMA of the constituent layers leading to the formation of 90° Néel domain walls for $T < T_{SR}$ and low IP fields; (**c**) for $T << T_{SR}$ and low IP fields the IP magnetic moment is vanishingly small, and (**d**) reorientation of LSMO spins back to IP for $T << T_{SR}$ and increasing IP field; (**e**) Model for SLs in the saturated state, at high IP magnetic fields exceeding the H_C of LMCO.

3.3. Magneto-Thermal Conductivity of LSMO/LMCO SL

To analyze the temperature and magnetic field behavior of thermal conductivity $\kappa(T, B)$ in LSMO/LMCO SLs, we first measured the cross-plane thermal conductivity of the constituting single films LSMO/STO(100) and LMCO/STO(100). The data on $\kappa(T, B)$ are shown in Figure 7. One can see that, throughout the measured temperature range, the thermal conductivity of the LSMO film either remains unchanged or increases under an applied magnetic field. This can be quantified by a positive magneto-thermal conductivity (MTC), which can be as large as $MTC(360 \text{ K}) = 100\% \times (\kappa(B) - \kappa(0))/\kappa(0) = +17\%$ at B = 5T. This value is definitely outside of the 2σ limit of ~2% (see Methods), making the MTC = 17%reasonable. Note that this MTC is confined to a relatively narrow temperature window close to T_{CLSMO} and seems to correlate with the CMR effect: Positive MTC values can be explained by a CMR-related field-induced increase of electrical conductivity in the LSMO film thereby increasing the electronic contribution to thermal conductivity and thus enabling MTC. However, an estimation of the pure electronic part of thermal conductivity by using the WF law accounts only for a small fraction of the total measured MTC (see Figure S8, ref. [37]). Note, that the WF law, more or less satisfactorily describing the behavior of conventional metals and failing already for more complex semiconducting [30] and nanocrystalline metallic [60] systems, must not be applicable for strongly correlated electron systems, i.e., LSMO. This probably indicates that other possible magnetic fieldinduced changes of (a) heat capacity; (b) magnons; (c) oxygen octahedral tilt angles, and (d) Jahn-Teller disorder [33,61] might contribute to MTC, but they are difficult to disentangle into separate contributions.



Figure 7. Temperature dependencies of the field-cooled cross-plane thermal conductivity of LSMO/STO(100) and LMCO/STO(100) single films with the thicknesses d = 100 nm and 25 nm, respectively, in applied in-plane magnetic fields, B = 0-5 T. The dashed line marks the position of the cubic-tetragonal transition of the STO substrate, $T_{\text{STO}} = 105$ K.

Double perovskite LMCO films on STO(100) with a monoclinic structure possess a higher degree of octahedral tilting (Mn-O-Co angle of $\varphi_{LMCO} = 154^{\circ}$ (ref. [54]), as compared to that in rhombohedral LSMO/STO(100) (Mn-O-Mn angle $\varphi_{LSMO} = 168^{\circ}$ (ref. [56]). In addition, the insulating behavior of the cation-ordered LMCO due to superexchange and the doubled unit cell led to a significantly lower thermal conductivity compared to that in LSMO (Figure 7). Further, no influence of magnetic field on thermal transport in LMCO is observable, which fits the absence of the CMR effect in Co/Mn-ordered double perovskites [62]. Finally, one can see in Figure 7 a clear peak in the thermal conductivity of LMCO around T = 105 K, i.e., close to the temperature of the structural (cubic-tetragonal) phase transition of the STO substrate. Considering the epitaxial character of LMCO/STO

films and strong elastic coupling to the substrate, this peak in κ (105 K) can be ascribed to a change in the LMCO strain state due to the structural phase transition in the STO substrate.

The temperature and magnetic field dependence of the cross-plane thermal conductivity of the [(LMCO₉)/(LSMO)₉]₁₁/STO(100) SL is presented in Figure 8. Remarkably ultralow thermal conductivity $\kappa_{SL}(300 \text{ K}) = 0.32 \text{ Wm}^{-1}\text{K}^{-1}$ has been obtained in this SL sample in zero field. Similar values were reported in the literature for bulk samples of all-inorganic vacancy-ordered double perovskites (e.g., $\kappa_{Cs2SnI6}$ (295 K) = 0.37 Wm⁻¹K⁻¹ (ref. [63]), Ruddlesden-Popper perovskites (e.g., $\kappa_{Cs2PbI2Cl2}$ (295 K) = 0.37 Wm⁻¹K⁻¹ (ref. [64]), or chalcogenides like Ag₂Se (κ_{Ag2Se} (300 K) = 0.29 Wm⁻¹K⁻¹ (ref. [65]).



Figure 8. (a) Field-cooled cross-plane thermal conductivity of the $[(LMCO)_9/(LSMO)_9]_{11}/STO(100)$ superlattice in different applied in-plane magnetic fields. The arrows mark the temperatures used for the field-dependent magneto-thermal conductivity (MTC). (b) Field-dependent MTC of the $[(LMCO_9)/(LSMO)_9]_{11}/STO(100)$ superlattice.

Considering the SL geometry with thermal resistances of LMCO and LSMO connected in series, the ultralow cross-plane thermal conductivity of the SL could, in principle, originate both from the LMCO and LSMO layers as well as from the LSMO/LMCO interfaces. Note, that both the LMCO and LSMO layers in the SL, being only 9 u.c. thick, could be much less thermally conducting than the LSMO and LMCO single films in Figure 7. This is in line with the reduction and variation of oxygen octahedral rotation tilt angles determined from high-resolution iDPC images of the $[(LMCO_9)/(LSMO)_9]_{11}/STO(100)$ SL shown in Figure S5 (SM). The obtained values for the Mn-O-Mn(Co) angles φ vary in the range of approximately $154^\circ < \varphi < 160^\circ$. Within the LMCO layers, the angles center at $\varphi_{SL-LMCO} \approx 154^\circ$ which is similar to bulk, while within the LSMO layers, the values reach $\varphi_{SL-LSMO} \approx 160^\circ$, having a stronger tilt compared to the bulk LSMO with $\varphi_{LSMO} \approx 166^\circ$ (ref. [46]). In between, the values smoothly change across the interfaces. We suspect that the observed modulations of the octahedral tilt angles along the growth direction and the stronger tilting of LSMO oxygen octahedra in the SL compared to bulk LSMO could be the origin of the ultralow thermal conductivity in the LSMO/LMCO SLs.

Two important features appear when applying an external magnetic field (Figure 8): (1) A shift of the thermal conductivity peak to higher temperatures and (2) the emergence of an unexpected negative MTC within the temperature region 185 K < T < 235 K (see Figure 8a). The shift of the thermal conductivity peak of the SL in applied fields towards higher temperatures can likely be explained by the shift of the magnetic (T_C) and electric (T_{MI}) transition temperatures towards higher values, which is common for perovskite FM manganites [66]. However, neither of the single manganite films has revealed a negative MTC. The field-dependent MTC of the n = 9 u.c. SL is shown in Figure 8b for selected temperatures. One can see a minimum negative MTC reaching as low as

 $MTC(210 \text{ K}, 3 \text{ T}) \approx -11\%$. For stronger fields of 4 T < *B* < 9 T, the amplitude of the negative MTC decreases and even almost changes sign for *B* = 9 T. A possible explanation for the observed behavior is the field-induced spin disorder within the LSMO layers promoted by the ESM formation. The spin disorder affects the charge carrier mobility due to enhanced spin scattering (cf. Figure 5d) and could thus result in a reduction of the electronic contributions to the thermal conductivity of the SL.

4. Conclusions

Superlattices of La_{2/3}Sr_{1/3}MnO₃/La₂CoMnO₆ (LSMO/LMCO) were epitaxially grown on SrTiO₃(100) substrates using the metalorganic aerosol deposition technique. Their magnetic behavior was shown to be governed by perpendicular magnetic anisotropy, originating from magnetically hard double perovskite LMCO layers. An exchange-spring magnetic coupling between LSMO and LMCO layers was observed, leading to a spin reorientation transition of LSMO at $T_{SR} = 260$ K. Applied in-plane magnetic fields enable control of the degree of spin disorder through continuous spin rotation within the soft magnetic LSMO layers towards their natural in-plane easy axis. Such field-controlled spin order/disorder was found to strongly influence both electrical and thermal transport in the SLs via spindependent scattering of charge carriers and their contributions to thermal transport in LSMO. The results obtained highlight the suitability of exchange-spring magnetic coupling within perovskite superlattices not only for achieving perpendicular magnetic anisotropy with nanoscale layer thicknesses down to ~9 u.c. (~3.5 nm) but also for controlling both electrical resistance and thermal transport using magnetic fields.

Supplementary Materials: The following supporting information can be downloaded at: https://www. mdpi.com/article/10.3390/nano13212897/s1. Figure S1: Left: Atomic force microscope topography of the $[(LMCO)_n/(LSMO_n)]_m/STO(100)$ n = 9 u.c. SL (RMS roughness S_q = 0.2(1) nm); Right: SL n = 24 u.c. (S_q = 0.5(1) nm; Figure S2: Left: XRR patterns (black curves) and fitting curves using the program GenX3 [40] of [LSMOn/LMCOn]m/STO(100) SLs revealing superstructure peaks of the bilayers. The fit parameters are listed in Table S1. Right: X-ray diffraction patterns of the SLs reveal a very similar out-of-plane lattice parameter $c \approx 3.852 \pm 0.004$ Å for all SLs and single LSMO and LMCO films. The arrows indicate the $k_{\alpha 1}/k_{\alpha 2}$ spliting of the STO(200) peak and of the (002) peak of most SLs; Table S1: GenX3 fit parameters for [LSMOn/LMCOn]m/STO(100) SLs; Figure S3: Distribution of Co (top, left) and Mn (top, right) atoms within the [(LMCO)₉(LSMO)₉]₁₁ SL obtained by using energy dispersive X-ray microanalysis (EDX) (left panels) shows a clear chemical contrast between the LMCO and the LSMO layers. A linear scan along the growth direction of the whole SL (bottom, left) and along the selected layers in the middle of SL (bottom, right), from which a (Co/Mn) intermixing at the LSMO/LMCO interfaces with a thickness ~2 u.c. can be deduced; Figure S4: Magnetic hysteresis loops for LSMO/STO(100) (left) and LMCO/STO(100) (right) at 5K along their respective easy axis; Table S2: Saturation magnetization and coercive field of LSMO/STO(100) and LMCO/STO(100) along their easy axis; Figure S5: Left: Field-cooled IP magnetic moment of the $[(LMCO)_n/(LSMO_n)]_m/STO(100)$ (n = 1–9 u.c.) superlattices at low magnetic field. Spin reorientation transition is missing in SLs with very thin LSMO and LMCO layers. Right: IP Magnetic hysteresis loops of selected [(LMCO)_n/(LSMO_n)]_m/STO(100) superlattices; Figure S6: ADF-STEM (top, left), iDPC (top, right) images of the [LSMO9/LMCO9]11/STO(100) superlattice, with the corresponding evaluation of octahedral tilt angles θ within the image plane (bottom). Connection to the Mn-O-Mn(Co) angle in the main text is done via $\varphi_{B-O-B} = 180^{\circ} - 2\theta$. The central cluster around $\theta = 0^{\circ}$ (on the right panel) corresponds to the Mn-Mn pairs, while the datapoints around $\theta = \pm 12^{\circ}$ correspond to the Mn-O-Mn(Co) bond chains. The analysis reveals continuous change of the octahedral tilt angle at the interfaces between LMCO ($\theta_{LMCO} \approx 13^{\circ}$) and LSMO ($\theta_{LSMO} \approx 10^{\circ}$). Error bars indicate the maximum scattering of the angles within one layer, while the standard deviation for all layers lies in the range of $\sigma(\theta) = 0.5-1.5^{\circ}$; Figure S7: Left: Raman spectra of the n = 24 u.c. SL [(LSMO)₂₄/(LMCO)₂₄]₄/STO(100) measured for different temperatures in the range $T \approx 100-400$ K and an illustration of the 644 cm⁻¹ breathing mode vibration; Right: Temperature dependence of the position of the breathing line (left scale) and IP magnetic moment (right scale) indicates a significant increase of the Curie temperature of the LMCO layers within the SL up to about $T_{C,LMCO} \approx 260$ K. The red line is a fit to the anharmonic line shift $\omega(T) = \omega_0 + C(1 + 2/(e^{\hbar\omega_0/2k_BT} - 1))$ [67] for temperatures T > T_{C,LMCO}; Figure S8: Electrical resistance vs. temperature (both current and magnetic field applied in-plane) in the vicinity of structural phase transition in STO at T* = 105 K for the $[(LMCO)_9/(LSMO_9)]_{11}/STO(100)$ SL at different magnetic fields. The arrows indicate the direction of the temperature scan; Figure S9: Top panel: measured magneto-thermal conductivity, MTC = $100\% \times [\kappa(5 \text{ T}) - \kappa(0)]/\kappa(0)$, (black points) and the estimated from the Wiedemann-Franz (WF) law for electronic contribution to MTC due to CMR (red points) of the single LSMO/STO(100). Bottom panel: colossal magnetoresistance CMR = $100\% \times [R(0) - R(5 \text{ T})]/R(0)$ of the LSMO/STO(100) thin film shows a typical behaviour with a peak close to $T_C \approx 350$ K. References [40,67] are cited in the Supplementary Materials.

Author Contributions: Lead of the project: V.M. Conceptualization and design of the study: V.M. and V.B.-B. Sample preparation and characterization: V.B.-B., I.W. and K.P.S. Transmission electron microscopy: V.R. and U.R. Thermal conductivity measurements and evaluation: V.B.-B. Raman spectroscopy: L.S. Manuscript: V.B.-B. with revisions by V.M. and I.W. All authors discussed the results and contributed to the final manuscript. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by German Research Foundation (DFG) within the CRC 1073 Projects A02 and Z02; DFG Projects MO-2255-4 and RO-5387/3-1, and International Center for Advanced Studies of Energy Conversion (ICASEC).

Data Availability Statement: The data presented in this study are available on request from the corresponding author.

Acknowledgments: The authors acknowledge the financial support by the German Research Foundation (DFG) within the CRC 1073 Projects A02 and Z02. We thank D. Steil and T. Titze for fruitful discussions. VB and KS gratefully acknowledge the financial support from the International Center for Advanced Studies of Energy Conversion ICASEC. V.M. and V.R. acknowledge the financial support by the DFG via Projects MO-2255-4 and RO-5387/3-1, respectively. V.R. acknowledges the European Regional Development Fund and the State of Brandenburg for the Themis Z TEM (part of the Potsdam Imaging and Spectral Analysis Facility (PISA)). The use of equipment in the "Collaborative Laboratory and User Facility for Electron Microscopy" (CLUE) www.clue.physik.uni-goettingen.de (accessed on 30 October 2023) is gratefully acknowledged.

Conflicts of Interest: The authors declare no conflict of interest.

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Article



Magnetic, Antiferroelectric-like Behavior and Resistance Switching Properties in BiFeO₃-CaMnO₃ Polycrystalline Thin Films

Abdelilah Lahmar ^{1,*}, Jacem Zidani ¹, Jamal Belhadi ¹, Ilham Hamdi Alaoui ¹, Hussam Musleh ², Jehad Asad ², Naji Al Dahoudi ² and Mimoun El Marssi ¹

- ¹ Condensed Matter Physics Laboratory (LPMC), University of Picardie Jules Verne, 33 Rue Saint Leu, 80000 Amines, France; jacem.zidani@etud.u-picardie.fr (J.Z.); jamal.belahdi@u-picardie.fr (J.B.); ilham.hamdi.alaoui@u-picardie.fr (I.H.A.); mimoun.elmarssi@u-picardie.fr (M.E.M.)
- ² Physics Department, Al Azhar University-Gaza, Gaza P.O. Box 1277, Palestine; drhussmu@gmail.com (H.M.); asaadjihad@gmail.com (J.A.); najialdahoudi@gmail.com (N.A.D.)
- * Correspondence: abdel.ilah.lahmar@u-picardie.fr; Tel.: +33-3-22-82-76-91

Abstract: The effect of ferromagnetic CaMnO₃ (CMO) addition to structural, magnetic, dielectric, and ferroelectric properties of BiFeO₃ is presented. X-ray diffraction and Raman investigation allowed the identification of a single pseudocubic perovskite structure. The magnetic measurement showed that the prepared films exhibit a ferromagnetic behavior at a low temperature with both coercive field and remnant magnetization increased with increasing CMO content. However, a deterioration of magnetization was observed at room temperature. Ferroelectric study revealed an antiferroelectric-like behavior with a pinched P–E hysteresis loop for 5% CMO doping BFO, resulting in low remnant polarization and double hysteresis loops. Whereas, high remnant polarization and coercive field with a likely square hysteresis loop are obtained for 10% CMO addition. Furthermore, a bipolar resistive switching behavior with a threshold voltage of about 1.8 V is observed for high doped film that can be linked to the ferroelectric polarization switching.

Keywords: ferromagnetic; antiferroelectric-like; polycrystalline films; BiFeO₃-CaMnO₃; resistance switching

1. Introduction

Interest in multiferroic materials has been steadily growing due to their interlinked electric, magnetic, and structural order parameters, resulting in concurrent ferromagnetic, ferroelectric, and magnetoelectric characteristics [1–3]. Among these materials, BiFeO₃ (BFO), which has been extensively investigated, exhibits ferroelectric behavior with a Curie temperature (TC) of 1083 K and G-type antiferromagnetic properties with a (TN) of 643 K [4,5]. Furthermore, it maintains a distorted rhombohedral structure within the (R3c) space group at room temperature, rendering it an appealing option for numerous technological applications [6,7]. A review of the literature has revealed that bulk BFO is susceptible to high leakage currents attributed to defects within its matrix [8,9]. However, BFO thin films have garnered increased attention due to reported enhancements in remnant polarization (Pr) and magnetization when compared to bulk single crystal [10]. Nevertheless, the low resistivity of BFO films can impede polarization switching, representing a significant concern primarily due to the complex defect chemistry [11–13]. It is important to note that reducing the grain size and appropriate doping can effectively mitigate leakage currents in BFO, improving its microstructure. Extensive research has been conducted to enhance the electrical and magnetic properties of BFO through doping strategies [8,14–22].

It is worth noting that significant progress has been made in showcasing the multifunctionality of BFO-based materials. Notably, researchers have reported intriguing

Citation: Lahmar, A.; Zidani, J.; Belhadi, J.; Alaoui, I.H.; Musleh, H.; Asad, J.; Al Dahoudi, N.; El Marssi, M. Magnetic, Antiferroelectric-like Behavior and Resistance Switching Properties in BiFeO₃-CaMnO₃ Polycrystalline Thin Films. *Materials* **2023**, *16*, 7392. https://doi.org/ 10.3390/mal6237392

Academic Editor: Jose Maria De Teresa, Ricardo Lopez Anton and Sion Federico Olive Méndez

Received: 15 October 2023 Revised: 5 November 2023 Accepted: 7 November 2023 Published: 28 November 2023



Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). enhancements in multiferroic properties in both epitaxial and polycrystalline BFO-based thin films. For instance, the incorporation of rare-earth elements into epitaxial BFO thin films has led to the emergence of a morphotropic phase boundary (MPB) between the rhombohedral phase (R3c) and orthorhombic phase (Pnma) at a critical composition of x = 0.14, particularly for elements such as Gd and Sm. In this composition range, distinctive features such as pinched hysteresis loops with small remnant polarization have been documented, indicating the presence of antiferroelectric-like behavior in these compositions [23,24]. Transmission electron microscopy investigations have provided corroborating evidence of local ordering, similar to what is observed in antiferroelectric (AFE) PbZrO₃ materials [25]. The observation of this region holds particular promise for achieving a significant piezoelectric response. However, it is important to note that the macroscopic response of these compositions continues to exhibit primarily ferroelectric behavior.

On the other hand, the phenomenon of resistance switching (RS) in BFO-based materials has garnered significant attention, particularly in the context of nonvolatile memory devices. Y. Shuai et al. reported nonvolatile bipolar resistive switching in Au/BiFeO₃/Pt configurations [26]. Additionally, Xinman Chen et al. documented bipolar RS behaviors in BiFeO₃ thin films with Pt/BiFeO₃/LNO setups [27]. The strategy of doping BFO has also emerged as a compelling avenue for enhancing RS properties. Yang C. H et al. observed such properties in Ca-doped BiFeO3 films, employing conductive atomic force microscopy [28]. Furthermore, Mi Li et al. reported RS behavior in metal/Bi_{0.95}La_{0.05}FeO₃/Ptsandwiched structures [29]. Through this brief literature review, it becomes evident that BFO-based materials continue to captivate researchers in the field of multiferroics due to their adaptability and multifunctionality. Notably, their physical and chemical properties can be readily adjusted to achieve desired characteristics.

Prior studies have demonstrated that the incorporation of RMnO₃ (where R represents a rare-earth element) into BFO thin films can effectively enhance both ferroelectric and magnetic properties, even at doping concentrations of up to 10% [30]. These investigations have revealed that even a minor doping concentration can instigate significant structural changes, characterized by the emergence of Jahn–Teller distortion. This structural transformation has been ascribed to the presence of Mn³⁺ ions within the BFO matrix [31]. However, it is noteworthy that the substitution of Bi³⁺ ions, which are stereochemically active lone pair ions, with lanthanide elements, which are nonstereochemically active ions, appears to lead to a reduction in the stereochemical activity of Bi–O bonds.

In pursuit of exploring additional functionalities and advancing our research on the impact of manganates on the physico-chemical properties of BFO polycrystalline films, our present study focuses on the influence of the manganite compound CaMnO₃. In our previous research, we extensively discussed the presence of Mn^{3+} ions occupying Fe³⁺ sites, demonstrating its critical role in maintaining a polarization switching behavior [30,31]. Conversely, the incorporation of Ca²⁺ ions into the Bi³⁺ sites has been noted as particularly intriguing for inducing a resistance switching behavior [32–34]. Additionally, Lu Liu et al. reported the coexistence of unipolar and bipolar resistive switching in Bi_{0.8}Ca_{0.2}FeO₃ polycrystalline thin films [32]. In this work, we place emphasis on the fabrication of BiFeO₃-xCaMnO₃ (Bi_{1-x}Ca_xFe_{1-x}Mn_xO₃ ($0 \le x \le 0.1$)) polycrystalline thin films and the comprehensive investigation of their structural, magnetic, and electrical properties. Remarkably, our findings reveal the presence of an antiferroelectric-like characteristic within our system, coexisting with a resistance switching behavior. This discovery holds significant promise for distinguishing between ferroresistive effects [9] and trapping phenomena [35].

2. Materials and Methods

Thin films were synthesized through a spin-coating process onto a commercial (111)-Pt/Ti/SiO₂/Si substrate heterostructure. The initial materials used were Bi-acetates and Sr acetates tetrahydrate (sourced from Alpha easer, Thermo Scientific Chemicals, Karlsruhe, Germany), as well as Mn, Fe, acetylacetonate (obtained from Sigma-Aldrich, Darmstadt, Germany). These compounds were dissolved in a mixture of propionic acid and 2-methoxyethanol in a volume ratio of 1:2, resulting in a sol concentration of 0.22 mol/L. Pyrolysis of the sol-gel was carried out on a hot plate set at 260 °C. Subsequently, a final annealing process was conducted within a preheated tube furnace under a saturated oxygen atmosphere at 650 °C for a duration of 60 min. The thickness of the resulting films after annealing was determined using scanning electron microscopy (SEM) on cross-sections. Microstructural analysis of the prepared samples was performed using an Environmental Quanta 200 FEG (FEI company, Hillsboro, Oregon, USA) microscopy (SEM) operating at 5 kV. The thin films obtained in this study underwent several characterization techniques. Firstly, X-ray diffraction analysis was carried out at room temperature using a four-circle high-resolution D8 Discover Bruker diffractometer equipped with a Göbel mirror. Cu K α radiation with a wavelength (λ) of 1.5418 Å was utilized for this analysis. Additionally, Raman spectroscopy was performed in a back-scattering configuration using a micro-Raman Renishaw spectrometer, with a green laser excitation source emitting at 514.5 nm. The laser power was carefully maintained below 20 mW to prevent any sample heating effects. For the assessment of magnetic properties, a commercial Physical Property Measurement System (PPMS DynaCool, Quantum Design) was employed. Magnetization measurements (M(T)) were conducted at both 2 K and 300 K, with an applied magnetic field up to H = 1 kOe. Dielectric measurements were carried out as a function of temperature and over a frequency range spanning from 100 Hz to 1 MHz. These measurements were performed using a Solartron Impedance/GAIN-PHASE analyzer SI-1260 (AMETEK scientific instruments, Oak Ridge, TN, USA), with a probing AC electric field amplitude of 100 mV. Ferroelectric investigations were conducted by measuring the polarization-electric field (P-E) hysteresis loops at a frequency of 10 kHz. A TF Analyzer 3000, aix-ACCT system, was employed for this purpose. To assess the leakage current properties, a Keithley 2611A source was utilized. All electrical measurements were executed using a metal-dielectricmetal geometry, with sputtered-Pt circular top electrodes featuring diameters of 250 µm. These electrodes were deposited through a shadow mask to ensure precise placement.

3. Results

3.1. Microstructural and Structural Investigation

Figure 1a,b present the scanning electron microscopy (SEM) images of the prepared thin films. In the case of the 5 CaBFOM phase, the microstructure reveals plate-like grains, with distinct grain boundaries that are readily visible. It is worth noting that as the concentration of doping elements increases, it results in the fragmentation of larger grains, leading to a noticeable reduction in grain size. The average grain sizes were measured to be 130 nm and 89 nm for the 5 CaBFOM and 10 CaBFOM thin films, respectively. It seems that the increasing of the CMO concentration inhibits the grain growth while sintering.

The EDX spectra carried out on both films showed the expected starting elements Bi, Fe, Ca, Mn, and O. Figure 1c shows an example of the EDX analysis carried out on 10 CaBFOM film. The average thickness of the prepared films was found to be approximately 280 nm (see Figure 1d as example). Figure 2 illustrates the X-ray diffraction (XRD) patterns of the films under investigation, with the reflections indexed based on a pseudocubic unit cell. All films exhibited pure perovskite phases, and these findings are considered accurate within the precision of the employed device. It is indeed challenging to discern detailed structural changes when transitioning from a 5% to a 10% CaMnO₃ concentration. Nevertheless, a noticeable trend emerges in favor of orientation in the (h00) direction when comparing the diffraction patterns. Remarkably, the splitting reflections (110) and (-110), which are observed in pure BFO with excess (Figure 2a), were not detected upon using 10% Bi excess or doping with $CaMnO_3$, as shown in Figure 2b. Instead, they appear to have merged into a single peak around 32° (2 θ), consistent with previous reports that have linked this phenomenon to structural transformations [30,31]. Additionally, upon closer examination of the position of the (100) reflection (as depicted in the inset), a clear shift towards higher angles is evident with an increase in the $CaMnO_3$ concentration to 10%. The lattice spacing, determined from the (100) pseudocubic peaks (d_{100} values), closely approximates the in-plane lattice spacing of Pt (100), which is 0.3923 nm. This alignment suggests a good lattice match between the prepared thin films and the Pt-crystal substrate as a possible contributing factor to these observations.



Figure 1. Surface morphologies of studied specimens: (**a**) 5 CaBFOM; (**b**) 10 CaBFOM; (**c**) example of EDX analysis for 10 CaBFOM film; and (**d**) example of cross-section for 10 CaBFOM film.



Figure 2. XRD pattern of (**a**) BFO thin films with and without Bi excess; (**b**) comparison of 5 CaBFOM and 10 CaBFOM thin films. All films are deposited on (111)-Pt/Ti/SiO₂/Si. Pt and Si denote peaks belonging to the substrate. The reflections are indexed according to a pseudocubic unit cell.

Raman spectroscopy was employed to gain further structural insights not accessible through X-ray diffraction (XRD). Figure 3 displays the Raman spectra of both studied films in comparison with that of the pure BFO thin film.



Figure 3. Raman spectra of the investigated thin films: (a) BFO for comparison, (b) 5 CaBFOM, and (c) 10 CaBFOM. The dotted line shows the shift of the mode with substitution.

Recall that in BFO bulk materials, the selection rules for the Raman active modes predicted 27, 13, and 8 modes for monoclinic, rhombohedral, and tetragonal symmetries, respectively. As depicted from the deconvolution of the Raman spectrum of BFO polycrystalline thin films, 18 vibration modes are founded, suggesting the monoclinic symmetry as reported by Kartopu et al. [36]. The assignment of each mode can also be found in this reference, noting that all observed modes below 300 cm⁻¹ were attributed to Bi–O covalent bonds. The substitution of Bi^{3+} by Ca^{2+} induced the decrease in the Bi–O, and all associated vibration modes become progressively weak. Additionally, two broad bands appear around 620 cm⁻¹ and within the range of 450 to 550 cm⁻¹, corresponding to symmetric and antisymmetric stretching modes, respectively. In comparison to pure $BiFeO_3$ (the parent phase), the presence of these bands is associated with the basal oxygen ions of the $Mn^{3+}O_6$ octahedra, which are linked to Jahn–Teller (JT) distortion with apparition of orthorhombic symmetry. Further discussion regarding the development of these features when doping BFO with rare-earth manganite can be found in our prior research [30,31,36,37]. For instance, Ca-doped BiFeO₃ bulk materials are successfully refined by assuming a mixture of the rhombohedral R3c and orthorhombic Pnma space groups in the work of Sunil Chauhan et al. [38]. Further, the authors reported that the contribution of orthorhombic phase increases with increasing Ca content in BiFeO₃ nanoparticles. Upon a closer look at obtained Raman spectra in the present work, it seems that the intensity ratio of the peak at 150 cm^{-1} (the most intense peak in BFO spectrum) with regard to the band appearing at 627 cm⁻¹ (the most intense peak in CaBFOM spectra) exceeds unity by increasing the concentration of CaMnO₃. It is very likely that at a high concentration, the structure changes from orthorhombic to tetragonal symmetry. Such a behavior was also observed in the $BFO-LaMnO_3$ system [31].

3.2. Magnetic Investigations

The magnetic hysteresis curves for the studied specimens at both room temperature (RT) and 2 K are presented in Figure 4. It is worth noting that CaMnO₃ is recognized as an antiferromagnetic insulator (AFMI) material, characterized by the presence of both four- and tri-valent manganese ions [39]. This manganite exhibits a complex magnetic behavior at low temperatures, transitioning from antiferromagnetic (G-type AFM) to paramagnetic ordering with a Neel temperature around 125 K and eventually revealing a weak ferromagnetic component below 10 K [40–42].



Figure 4. Magnetic hysteresis loop for the investigated thin films (a) at 300 K; (b) at 2 K.

The strong G-type antiferromagnetic (AFM) order observed at 120-125 K in CaMnO3 is attributed to superexchange interactions between Mn^{3+} and Mn^{4+} ions. Conversely, the ferromagnetic (FM) order in CMO arises from the presence of double exchange interactions [43,44]. In the present study, as depicted in Figure 4a, there is no significant improvement in magnetization observed at room temperature when compared to what is observed for the BFO thin film [9]. However, a decrease in magnetic properties is evident when increasing the CMO content from 5% to 10% at room temperature. Similar behavior was reported with the addition of $LaMn_{0.5}Co_{0.5}O_3$ to BFO thin films [45]. Interestingly, the influence of CMO addition on magnetization becomes more pronounced at low temperatures. As shown in Figure 4b, clear ferromagnetic hysteresis is observed for both investigated films. Notably, the increase in CMO content results in an elevation of the magnetic coercive field from 900 Oe for 5 CaBFOM to 1440 Oe for 10 CaBFOM films, but with maintaining almost the same value of remnant magnetization of 2.50 emu/cm³, which indicates that the material becomes magnetically hard. However, the saturation magnetization decreased by half with increasing CMO content from 5 to 10%. This behavior is plausible when considering that the increase in CMO content leads to a change in the composition, thus the increase in corresponding magnetic interactions, leading probably to the increase in the anisotropy magnetic field.

3.3. Dielectric and Ferroelectric Investigation

In order to investigate the impact of CaMnO₃ doping on the dielectric and ferroelectric properties of BiFeO₃, we conducted measurements of dielectric permittivity and polarization on both of the studied samples in comparaison with the data reported for pure BFO.

In Figure 5, we present the dielectric permittivity and losses as functions of frequency at room temperature for BFO, 5 CaBFMO, and 10 CaBFMO samples. Initially, the pure BFO shows almost a linear dielectric constant around 100 until 10^5 Hz and then drops down (Figure 5a). This behavior is due to the existence of interface states originating from the contact between the thin film and electrode during the elaboration of the BFO thin film. Indeed, during the measurement, the interfacial charge trapped is enabled to follow the

alternating current variations at a high frequency, giving rise to a small dielectric constant at high frequencies. Similar behavior is reported in some Bi-based thin films [46,47]. It is also observed at the same time that the dielectric loss increases suddenly at a high frequency, which could be derived from the polarization relaxation of the inherent electric moment in $BiFeO_3$ or from the displacement polarization of different valence ions [48]. Note that the internal interfacial barrier or electrode effects have been pointed out by Shao Wei Wanga et al. [47] as a possible cause for such behavior. It is evident from Figure 5b that the 5 CaBFOM sample exhibits a consistent decrease in the dielectric constant as the frequency increases. Concurrently, the dielectric losses are notably higher at lower frequencies but decrease significantly as the frequency rises, reaching a minimum value of 0.05. These findings are indicative of space charge activation at lower frequencies, a well-known phenomenon in BFO-based materials. At the high frequency, it behaves similarly to the pure BFO with an increase in dielectric losses between 10^5 and 10^6 Hz. For the 10 CaBFOM thin film, and as is depicted in Figure 5c, the frequency dispersion of the dielectric constant is more pronounced because the increase in the CMO amount induced a change in the chemical gradients in the thin film, thus showing more relaxation phenomena. The dielectric loss until 10^6 Hz seems to decrease considerably, but it is likely that the branch of increase in dielectric losses might be observed in the MHz frequency zone. Comparably, the dielectric permittivity of the 5 CaBFMO sample is approximately two times higher than that of the 10 CaBFMO sample. This difference can be attributed to domain pinning resulting from the presence of dipole defects (further discussed below).



Figure 5. Room temperature frequency dependence of the constant dielectric and the dielectric losses for (a) BFO thin film, (b) 5 CaBFOM thin film, and (c) 10 CaBFOM.



Figure 6a,c showcase the ferroelectric P-E hysteresis loops measured at room temperature for the 5 CaBFMO and 10 CaBFMO films at various frequencies. The hysteresis loops of BFO with and without excess were given for comparison.

Figure 6. Room temperature polarization hysteresis P-E loops for (**a**,**b**) BFO without and with 10% Bi excess; (**c**) 5 CaBFMO at different frequencies; (**d**) 5 CaBFMO at 10 kHz with the corresponding polarization current switching; (**e**) 10 CaBFMO at different frequencies; and (**f**) 10 CaBFMO at 10 kHz with the corresponding polarization current switching.

It is well known that the defect chemistry in BFO is related mostly to the volatility of Bi that created Bi vacancies. In this case, oxygen vacancies may form for compensation (using Vink–Kröger notation):

$$2Bi_{Bi} + 3O_O = 2V_{Bi}''' + 3V_{\ddot{O}} + Bi_2O_3$$

The high leakage current and conductivity hindered the switching polarization for the pure BFO, as is shown Figure 6a, noting that similar behavior is reported for some Bi-based materials [49]. However, the excess of 10% Bi may create donor states that could compensate oxygen vacancies and lead to an overall improvement of the electrical properties. In such a case, polarization switching is not hindered, as can be depicted from Figure 6b. Albeit, the P-E loop still shows some irregularity. It is worth noting that co-doping is shown to be a good strategy to improve BFO functionality [49].

Concerning CMO-modified BFO thin films, the ionization of oxygen vacancies yields electrons to compensate hole carriers created by Ca^{2+} for maintaining the highly stable Fe^{3+} , as in the case of Ca-doped BiFeO₃ [28]. Figure 6c,e show that both samples exhibit fully

saturated P-E loops with a remarkably high maximum polarization exceeding 40 μ C/cm². It is important to note that we observe an enhancement in maximum polarization as frequency decreases. This increase can be attributed to the impact of leakage currents, which become more prominent at lower frequencies, as evidenced in the dielectric measurements. Another noteworthy observation is that the 5 CaBFMO film exhibits a clear double P-E loop. Figure 6d,f depict the P–E loops and their corresponding polarization current switching measured at 10 kHz for the 5 CaBFMO and 10 CaBFMO films, respectively. The polarization current curves for both films reveal the presence of four switching current peaks, a characteristic indicative of AFE or non-ergodic states. The observed AFE character can be attributed to the formation of various defect dipoles involving oxygen and cation vacancies, aimed at achieving charge balance within the material. In ferroelectrics, ordered defect dipoles can act as pinning centers within domains, impeding the switching of ferroelectric domains when exposed to an externally applied electric field [50,51]. It is worth noting that the electric field corresponding to the current peak I_1 , which signifies the transition from antiferroelectric-like to ferroelectric behavior (AFE-FE), is twice as high in the 5 CaBFMO film compared to the 10 CaBFMO film. This observation implies that the static electric field generated by dipole defects is stronger in the 5 CaBFMO film. This higher internal static electric field can hinder long-range polar order, resulting in a lower remanent polarization with clear antiferroelectric (AFE)-like behavior observed in the 5 CaBFMO film. This phenomenon can explain the lower dielectric permittivity observed in the 5 CaBFMO film due to increased domain pinning.

In their theoretical work, Bin Xu et al. [52] reported that the pinched loop is probable when FE and AFE are very close to each other in energy at morphotropic phase boundaries (MPBs). The authors surmise that this type of behavior occurs in the so-called hybrid improper ferroelectrics where a larger anti-polar amplitude and a small finite polarization exist simultaneously.

It is important to mention that the generation of a double hysteresis loop in ferroelectric $BiFeO_3$ materials has potential applications in innovative nanodevices, including high-density multistate data storage [50]. This property opens up opportunities for exploiting the unique characteristics of these materials in advanced technological applications.

3.4. Resisting Switching Behavior

Electrical measurements have revealed that all of our samples exhibit resistive switching behavior without the need for any forming process. Figure 7 displays the current–bias (IV) curve for Pt/CaBFMO/Pt films, with a maximum applied voltage of 6 V. The obtained IV curves are nearly symmetric. In the case of Pt/5 CaBFMO/Pt, shown in Figure 7a,c, a weak hysteresis is observed in the positive voltage polarity. It is important to note that this film exhibits antiferroelectric-like behavior, typically attributed to an internal bias field established by defect dipoles. These results suggest that charge carriers localized near interfaces do not contribute significantly to the resistive switching. It is known that Mn doping can significantly reduce leakage current in BFO films and enhance ferroelectric polarization. Several studies have demonstrated that ferroelectric polarization charges can control resistive switching in BFO thin films [53]. In this case, the 5% CMO content incorporated into the BFO matrix does not result in a fully saturated ferroelectric hysteresis loop and does not induce resistive switching either. Therefore, it appears that no charge-trapping effect is prominent in this film.

However, in the case of the Pt/10 CaBFMO/Pt film (Figure 7b,d), where the CMO concentration is 10%, the scenario is different.

In the case of the Pt/10 CaBFMO/Pt film, the resistive switching behavior is notable. Initially, the BFO film is in a high-resistance state, and at around 1.8 V, the film switches to a low-resistance state. The resistance ratio (Δ R) obtained for the positive bias region, as indicated by the blue arrow, demonstrates a change of approximately three orders of magnitude. The resistance ratio deduced from this figure is roughly 10³, which is a high value comparable to that reported in similar systems [54]. This high value positions our



film as a promising candidate for nonvolatile resistive memories, as a resistance ratio of 10 is typically considered competitive with Flash technology [55,56].

Figure 7. IV characteristics of (**a**) 5 Ca BFMO thin film; (**b**) 10 Ca BFMO thin film; (**c**,**d**) represent the IV at different applied biases for 5 CaBFOM and 10 CaBFOM, respectively.

It is important to note that this bipolar resistive switching, with a threshold voltage (the set tension) of about 1.8 V (indicated by the red dashed line in Figure 7b), can be directly related to the ferroelectric polarization observed in this film. However, it is worth mentioning that the current hysteresis in our case is not perfectly antisymmetric. In fact, the resistance ratio obtained in the negative bias region is smaller. This suggests that interfaces play a relatively smaller role in resistance switching compared to the impact of ferroelectric polarization in our system.

4. Conclusions

In summary, the addition of CaMnO₃ had significant effects on the structural, magnetic, and electrical properties of BFO thin films. Magnetic investigations revealed that the magnetic characteristics of BFO were strongly influenced by CaMnO₃, resulting in a ferromagnetic order at low temperatures and an antiferromagnetic order at room temperature. In the ferroelectric study, the 5 CaBFMO film displayed a pinched hysteresis loop, while the 10 CaBFMO film exhibited a well-saturated loop. Intriguingly, the polarization current curves for both films displayed the presence of four switching current peaks, characteristic of antiferroelectric-like behavior. It appears that the co-doping of Ca and Mn into the BFO matrix induced changes in the cation ordering at the A-/B-sites, leading to local structural heterogeneity that varied with the concentration of CaMnO₃. Additionally, reversible resistive switching was observed in the 10 CaBFMO film when an electric field was applied. Overall, the co-doping of BFO with Ca and Mn (CaMnO₃) shows promise for enhancing the functionalities of BFO materials, opening up opportunities for advanced applications and novel device technologies.

Author Contributions: Conceptualization, A.L.; validation, M.E.M., J.B. and N.A.D.; formal analysis, I.H.A., J.Z. and J.A.; investigation, A.L., J.Z., I.H.A. and H.M.; data curation, H.M., J.B. and J.A.; writing—original draft preparation, A.L.; writing—review and editing, A.L., M.E.M., J.B. and N.A.D. All authors have read and agreed to the published version of the manuscript.

Funding: Financial support of this work was provided by the PHC AL MAQDISI 2021 grant No. 48024ZF.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Data are contained within the article.

Acknowledgments: Hussam Musleh would like to thank the "Ambassade de France à Jérusalem" for Scientific High-Level Visiting Fellowships (SSHN) 2023.

Conflicts of Interest: The authors declare no conflict of interest.

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Agata Kraśkiewicz and Agnieszka Kowalczyk *

Department of Chemical Organic Technology and Polymeric Materials, Faculty of Chemical Technology and Engineering, West Pomeranian University of Technology in Szczecin, 70-322 Szczecin, Poland; agata.kraskiewicz@zut.edu.pl

agata.kraskiewicz@zut.edu.pi

* Correspondence: agnieszka.kowalczyk@zut.edu.pl

Abstract: In the presented study, UV LEDs (365 nm) or a medium-pressure mercury lamp (UV-ABC) were verified as UV radiation sources initiating the photocrosslinking process of varnishes based on novel photopolymerizable phosphorus (meth)acrylate oligomers. Coating formulations were composed of (meth)acrylic/styrene telomers with terminal P-atoms (prepared via a UV phototelomerization process) and different photoinitiators (HAPs, APOs, or APO blends). The kinetics of the UV crosslinking process of the coating formulations depending on UV irradiation and the UV range was investigated by the photo-DSC method. Moreover, the hardness of the varnishes and the conversion of double bonds using the FTIR method were tested. The photopolymerization rate and the photoinitiator index, depending on the type of photoinitiator, were as follows: APOs < APO blends < HAPs. However, the highest coating hardness results were obtained using the least reactive photoinitiator from the APO group, i.e., Omnirad TPOL, or a mixture of three different types of acylphosphine (Omnirad BL 750). The greater effectiveness of the above-mentioned APOs over HAP was also demonstrated when using a UV LED lamp at 365 nm with a low UV dose and UV irradiance, thanks to the presence of phosphoric acid diester in the coating composition, acting as both a telogen and an antioxidant.

Keywords: phosphorus-containing coatings; telomerization; UV curing; (meth)acrylates; LED

1. Introduction

UV radiation curing is becoming increasingly appreciated at present. The growing interest in this technology is related to its ecological and economic benefits, such as high process rates at room temperature, low volatile organic compound (VOC) emissions, and the use of solvent-free formulations [1–4]. The application areas of UV-curable materials include electronics [5], aerospace [6], packaging [7], and the wood industry [8], as well as medicine [9] and dentistry [10].

The most common radiation sources used in UV curing technology are mediumpressure mercury lamps. Their popularity is mainly due to the emission of three types of UV radiation (UV-A, UV-B, and UV-C) and relatively low prices. However, some limitations are also noticeable, e.g., the production of harmful ozone, toxic mercury content, a short lifetime (approximately 1500–2000 h), high energy consumption, and an intensive temperature rise [11–13]. In addition, it is important to take into account that the EU has imposed restrictions on the production of mercury-containing lamps from 2027 [14]. For these reasons, promising sources of UV radiation are UV-LEDs. The longer lifetime, elimination of mercury, and no ozone generation make them inherently environmentally friendly. In addition, both their 50% lower energy consumption (due to the possibility of immediate switching on/off or their use only when necessary, and their narrow wavelength distribution) and their suitability for heat-sensitive materials further encourage the replacement of UV mercury lamps with UV LED systems [15–17].

Citation: Kraśkiewicz, A.; Kowalczyk, A. Radiation Curing of Phosphorus Telomer-Based Coatings Using UV LEDs or Medium-Pressure Mercury Lamp. *Materials* **2023**, *16*, 7493. https://doi.org/10.3390/ ma16237493

Academic Editors: Jose Maria De Teresa, Ricardo Lopez Anton and Sion Federico Olive Méndez

Received: 3 November 2023 Revised: 30 November 2023 Accepted: 1 December 2023 Published: 4 December 2023



Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). Typical photopolymerizable coating formulations are composed of multifunctional monomers or/and oligomers, photoinitiator(s), and reactive diluents [18]. The type and concentration of ingredients depend on the desired properties of the final products. (Meth)acrylate-functionalized oligomers and monomers are frequently used due to their high reactivity and thus wide modification possibilities [19]. In this context, particularly interesting are phosphate (meth)acrylates and poly(meth)acrylates—they allow the formation of coatings marked by unique properties, e.g., good adhesion to steel substrates [20], corrosion resistance [21], fire resistance [22], and antimicrobial resistance [23].

Syntheses of (meth)acrylate copolymers bearing functional groups—for example, with phosphorus atoms—have been carried out mainly via free radical polymerization techniques (or even via photopolymerization) [24]. It is also worth mentioning that the preparation of oligomers/polymers suitable for specific applications (well-defined copolymers) requires conducting controlled polymerization, e.g., atom transfer radical polymerization (ATRP) [25], reversible addition–fragmentation transfer process (RAFT) [26], or nitroxide-mediated radical polymerization (NMP) [27].

However, a less frequently described method of preparation for copolymers with controlled structures is telomerization-a special type of polymerization consisting of a chain reaction between a telogen (also called a chain transfer agent, a molecule with easily radically cleavable bonds, e.g., P-H, C-Br, S-H) and one or more polymerizable compounds (taxogens/monomers, exhibiting ethylenic unsaturation), which leads to the synthesis of low-molecular-weight oligomers with terminal groups derived from telogen [28,29]. Regarding the synthesis of phosphorus-containing oligomers by telomerization, dialkyl phosphites, phosphorus acid, phosphorus tri- and pentachloride, and alkyl dichlorophosphines or dichlorophosphonates are typically used as telogens. However, phosphate esters (e.g., dimethyl phosphate—proposed in these studies) are described in the literature reports as less effective chain transfer agents. Furthermore, the majority of reported telomerization reactions involving organophosphorus compounds are thermally initiated [30]. As stated, the preparation of phosphorus-containing telomers (oligomers) by UV-induced telomerization has not been noted thus far (apart from the work of authors [31]). The novelty of this type of coating is that they are obtained in an environmentally friendly way (without the use of organic solvents, with low demand for electricity and quickly). Photochemically induced telomerization allows the preparation of (semi)telechelic oligomers containing P-atoms in their structure (P-telomers). The authors' previous works presented in detail a new method of obtaining acrylate oligomers containing phosphorus, a comparison to other preparation methods, and the specific properties of the coatings obtained from these P-telomers [32].

In this study, the influence of the type of radiation source (medium-pressure mercury lamp or UV LEDs) and the photoinitiator (acylophosphine oxides or α -hydroxyalkylphenones) on the UV curing process, as well as the hardness of coatings based on phosphorus-containing (meth)acrylic resins (e.g., P-telomer syrups), were investigated.

2. Materials and Methods

2.1. Materials

The (meth)acrylic syrup containing phosphorus telomers (the P-telomer syrup, P-TS) was synthesized using the following monomers (a–d), P-telogen (e), and radical photoinitiator (f):

- (a) n-butyl acrylate (BA; BASF, Ludwigshafen, Germany);
- (b) methyl methacrylate (MMA; Sigma Aldrich, Steinheim, Germany);
- (c) 2-hydroxyethyl acrylate (HEA; Across Organics, Geel, Belgium);
- (d) styrene (STY; Sigma Aldrich, Steinheim, Germany);
- (e) dimethyl phosphite (DMPh, Sigma Aldrich, Steinheim, Germany);
- (f) bis(2,4,6-trimethylbenzoyl)-phenylphosphineoxide (Omnirad 819, IGM Resins, Waalwijk, The Netherlands).

The UV-curable varnish compositions were prepared using the P-telomer syrup (P-TS) and commercial type I radical UV photoinitiators (IGM Resins, Waalwijk, The Netherlands).

- α-Hydroxyalkylphenones (HAPs):
 2-hydroxy-1-[4-[4-(2-hydroxy-2-methylpropionyl)benzyl)phenyl)-2-methylpropan-1one (Omnirad 127);
 1-hydroxycyclohexylphenyl ketone (Omnirad 184).
- (ii) Acylphosphine oxides (APOs):
 - 2,4,6-trimethylbenzoyl-diphenyl phosphine oxide (Omnirad TPO);
 - ethyl(2,4,6-trimethylbenzoyl)-phenyl phosphinate (Omnirad TPO-L);
 - bis(2,4,6-trimethylbenzoyl)-phenylphosphine oxide (Omnirad 819).
- (iii) Blends of APOs:
 - a blend of bis(2,4,6-trimethylbenzoyl)-phenylphosphine oxide (ca. 95 wt%) and ethyl(2,4,6-trimethylbenzoyl)-phenyl phosphinate (ca. 5 wt%) (Omnirad 2100);
 - a blend of ethyl(2,4,6-trimethylbenzoyl)-phenyl phosphinate (ca. 60 wt%), 2,4,6-trimethylbenzoyl-diphenyl phosphine oxide (ca. 20 wt%), and bis(2,4,6-trimethylbenzoyl)-phenylphosphine oxide (ca. 20 wt%) (Omnirad BL 750).

The chemical structures of the tested photoinitiators (PIs) are shown in Figure 1.



Figure 1. Chemical structures of the tested PIs: Omnirad 127 (a), Omnirad 184 (b), Omnirad TPO (c), Omnirad TPOL (d), Omnirad 819 (e), Omnirad 2100 (f), Omnirad BL750 (g).

2.2. Preparation of the P-Telomer Syrup, Varnish Compositions, and Coatings

The P-telomer syrup (P-TS) was synthesized via the UV-induced telomerization (phototelomerization) process of the monomer mixture (BA, MMA, HEA, STY), the P-telogen (DMPh), and the radical photoinitiator (O819). The phototelomerization was carried out at 50 °C for 50 min in a glass reactor (250 mL) equipped with a mechanical stirrer, a water cooler, a thermocouple, and a capillary dosing inert gas (Ar). The UV LED stripe ($\lambda = 390 \pm 5$ nm; MEiSSA, Warsaw, Poland) was used as a UV light source. The composition of the reaction mixture is shown in Table 1, while the schematic structure of the phototelomerization reaction is shown in Figure 2.

Table 1. Reaction mixture used for the preparation of the P-telomer syrup (P-TS).

Monomers (wt%)				P-Telogen (wt. parts)	PI (wt. parts)	
BA	MMA	HEA	STY	DMPh	O819	
40	35	15	10	1.65	0.75	



Figure 2. Phototelomerization process of BA, MMA, HEA, and STY monomers with DPMh as P-telogen.

The UV-curable varnish compositions were prepared by the mechanical mixing of the P-TS and the selected radical photoinitiator (HAP, APO, or APO blend). Seven coating compositions were obtained (Table 2).

	Components					
Varnish Symbol	P-TS (wt. parts)	Photoinitiator				
		Symbol	Dose (wt. parts)	Dose (mol) *		
V-127		O127		0.00294		
V-184		O184		0.00489		
V-TPO		OTPO		0.00287		
V-TPOL	100	OTPOL	1	0.00316		
V-819		O819		0.00238		
V-2100		O2100		0.00243		
V-BL750	V-BL750			0.00291		

Table 2. The compositions of the UV-curable varnishes.

* mole/100 wt. parts of P-TS.

Then, they were stored for 24 h in a dark place and applied onto glass substrates using a gap applicator (60 μ m) and UV-irradiated by means of a medium-pressure mercury lamp at 200–420 nm (UV-ABC, Hönle UV-Technology, Gräfelfing, Germany; total UV dose of 6 J/cm²) or UV LEDs at 365 nm (own production; UV dose of 6 or 30 J/cm²). A schematic illustration of the varnish preparation is given in Figure 3.



Figure 3. Schematic illustration of the varnish preparation (M—monomer; R—radical, (CH₃O)₂PH is P-telogen).

2.3. Characterization of the P-Telomer Syrup

The P-telomer syrup was characterized in our previous publication (Table 3, [31]). The dynamic viscosity (η) was measured at 25 °C using the DV-II Pro Extra viscometer (spindle #7, 50 rpm; Brookfield, New York, NY, USA). The solid content (SC) was determined with a thermobalance (Radwag, Warsaw, Poland); during the measurement, samples (ca. 2 g) were heated in aluminum pans at 105 °C for 4 h. Monomers and telogen conversions were evaluated by proton nuclear magnetic resonance ¹H NMR and P NMR (Bruker DPX Avance III HD Spectrometer; 400 MHz); a solution of the P-TS in CDCl₃ was used. The required parameters were characterized by comparing the intensities of the monomers' peaks and the internal standard's (1,3-dinitrobenzene) peaks [32]. Gel permeation chromatography (GPC) was used for the evaluation of the molecular masses (M_w , M_n) and polydispersity (PDI) of the dry P-telomers (P-telomer syrup was heated at 140 °C for 4 h before the test to remove unreacted monomers).

Table 3. Properties of the P-telomer syrup and dry P-telomers.

SC (%) *	η (Pa·s)	M _n (g/mol)	M _w (g/mol)	PDI (a.u.) –	Monomer/Telogen Conversion (%) *				
					BA	MMA	HEA	STY	DMPh
47	1.2	14,300	48,300	3.4	27	64	30	77	30
									-

*—according to NMR data.

2.4. Kinetic Studies of UV Curing of the Varnish Composition

The kinetic studies of the photocuring processes, i.e., the reaction rate (R_p , W/g) and photoinitiation index (I_p , s⁻²), were determined using the photo-DSC method (a differential scanning calorimeter with UV equipment; Q100, TA Instruments, New Castle, DE, USA). The samples (varnish compositions, ca. 5 mg) were polymerized in open aluminum pans under isothermal conditions at 25 °C in high-purity nitrogen purged with 50 mL·min⁻¹ before and during the polymerization reaction. The polymerization was initiated with a UV lamp in three variants: (1) λ = 365 nm, I₀ = 90 mW/cm²; (2) λ = 250–450 nm, I₀ = 90 mW/cm²; (3) λ = 250–450 nm, I₀ = 500 mW/cm². The UV polymerization conditions were similar to those of the UV curing process, realized with a UV-ABC-type medium-pressure mercury lamp or UV LEDs. The above-mentioned parameters (R_p , I_p) were calculated according to Equations (1) and (2), respectively. In the calculations, the amounts of unreacted monomers indicated by NMR studies were taken into account.

$$R_p = \frac{\left(\frac{dH}{dt}\right)}{m} [W/g] \tag{1}$$

$$I_p = \frac{R_p^{max}}{t_{max}} \left[s^{-2} \right] \tag{2}$$

where dH/dt—the recorded heat flow during UV irradiation; *m*—the mass of the sample; R_p^{max} —the maximum polymerization rate calculated based on the theoretical heat value for the complete degree of conversion; t_{max} —the time to reach the maximum polymerization rate [31].

2.5. Characterization of the Varnishes

The basic mechanical property of the coatings—the pendulum hardness—was determined using a König pendulum (AWS-5, Dozafil, Warsaw, Poland) according to the PN-EN ISO 1522 standard (five measurements for each sample were performed) [33].

The degree of crosslinking of the varnish coatings was checked using a Fourier transform infrared spectroscope with ATR accessories (Nicolet 380, ThermoScientific, Waltham, MA, USA). The conversion of double bonds ($DC_{c=c}$) was calculated according to Equation (3). The DC was evaluated by the comparison of the area of the C=C stretching vibration bands at 1635 cm⁻¹ (the absorption bands of vC=C [34]) and at 812 cm⁻¹ (bond torsion vibration -C=CH₂ [35]) with the area of the C=O stretching vibration band at 1724 cm⁻¹.

$$DC_{c=c} = \left(1 - \frac{\frac{A_t^{812} + A_t^{1655}}{A_t^{7224}}}{\frac{A_0^{812} + A_0^{1655}}{A_0^{1724}}}\right) \cdot 100 \ [\%]$$
(3)

where A_0 is the initial intensity of the peak at a specific wavenumber and A_t is the intensity of the peak at the same specific wavenumber after the UV curing process.

3. Results and Discussion

3.1. Kinetic Studies of UV Curing of the Varnish Composition

The polymerization kinetics of varnish compositions with different PIs and UV curing conditions were followed by photo-DSC. In the study, systems containing HAPs, APOs, or APO blends were compared. It is worth noting that the weight addition of PIs was the same, i.e., 1 wt. part (industry practice was adopted in the study), while the molar concentration varied (about 0.003 mol/100 g of photoreactive mixture for all PIs; in the case of O184, ca 0.004 mol) (Table 2). It should also be mentioned that the photoreactive mixture was a telomeric syrup consisting of approximately 50% (meth)acrylate-styrene oligomers containing terminal phosphorus atoms (SC = 47%). Based on the NMR analysis, DMPh (as P-telogen) was incorporated into the oligomer's structure in about 30%. The remainder of the DMPh was in the P-TS. Therefore, during the UV irradiation of the coating composition
(P-TS + PI), not only the photopolymerization of unreacted monomers but also (to some extent) phototelomerization occurred (Figure 3). Thus, a mixture of unreacted monomers and P-telogen was involved in the photopolymerization (and phototelomerization) process, which consisted of 53% BA, 23% MMA, 19% HEA, and 5% STY (calculated from NMR). The process of creating a poly(meth)acrylate network in the coating takes place in the presence of linear oligomers with terminal P-atoms, which act as steric hindrances. The resulting cured coating is therefore a three-dimensional polymer network consisting of interconnected (entangled) macromolecules (without covalent nodes). The study aimed to demonstrate whether matching the type of photoinitiator in terms of its electromagnetic radiation absorption capacity to the characteristics of the radiation source, i.e., the range of wavelengths emitted, is as important for the photopolymerization process as is commonly believed. A particular case of photopolymerization is considered here, i.e., in the presence of an organophosphorus compound as a chain transfer agent (phototelomerization). As previously mentioned, the exposure of the samples was carried out in three variants in the photo-DSC chamber, reflecting the actual exposure conditions of the varnish—namely, with low UV irradiance (90 mW/cm²) and a specific wavelength, i.e., 365 nm or in the broad UV range (250-450 nm) (variants one and two, respectively), and with high UV irradiance and a broad UV range (variant three). The kinetic curves of systems irradiated at low UV irradiance, i.e., 90 mW/cm² (Figure 4a,b), are similar in some respects. Namely, the maximum reaction rates are between 4 and 8 W/g, regardless of the UV range. Only in the case of O184, the R_p^{max} value is higher, at approximately 10 W/g (which in turn is caused by the higher molar concentration of this photoinitiator; see Table 2). In contrast, for systems irradiated at high irradiance (500 mW/cm²), the R_p^{max} values are twofold higher (8 to 16 W/g). As can be seen, at high UV irradiance, the photopolymerization process occurs much faster, i.e., approximately 30 s for APOs and APO blends and approximately 45 s for HAPs (Figure 4c).



Figure 4. UV curing reaction rates for the varnish compositions in different UV curing conditions: (a) 365 nm, $I_0 = 90 \text{ mW/cm}^2$; (b) 250–450 nm, $I_0 = 90 \text{ mW/cm}^2$; (c) 250–450 nm, $I_0 = 500 \text{ mW/cm}^2$.

This is because, as is well known, the rate of photopolymerization initiation depends on the intensity of absorbed light (I_a), which corresponds to the number of photons absorbed per unit volume and time. The intensity of the absorbed light (I_a) depends on the intensity of the incident light (I_0), i.e., that emitted by the radiation source used, and on the absorbance of the photoinitiator. The latter, in turn, depends on the photoinitiator concentration and the thickness of the layer being exposed. In the results presented here, it can be assumed that the thickness of the irradiated layer is the same for each sample (approximately 5 mg of the sample was fed into standardized aluminum crucibles). To some extent, it can be considered that the molar concentration of the photoinitiator is the same (except for O184). Thus, the kinetic curves considered describe well the kinetics of the process as a function of the incident light intensity (I_0). The longest photopolymerization times were recorded when irradiated in the broad UV range (250–450 nm) and at low irradiance (90 mW/cm²); see Figure 4b. They were approximately 105 to 145 s (for systems with HAPs) and 60 to 120 s (for APOs and blends of APOs), respectively. The HAPs had strong absorption in the short-wave UV range (230-270 nm) and in moderate concentrations. They also had weak absorption at longer wavelengths of up to 360 nm. They are mainly used in clear coatings and produce hard coatings and are less suitable for styrene formulations due to their longer triplet lifetimes. Therefore, the highest reaction rate with a high UV irradiance value was recorded for the system with O184 (Figure 4c). Interestingly, in a wide range of UV radiation and at low irradiance (Figure 4b), the photopolymerization rate values for systems with HAPs (O184 and O127) were at an average level (approximately 6 W/g) and were higher than for APO mixtures, but the time needed to achieve R_p^{max} was the longest (over 60 s). Photopolymerization with HAPs occurred much faster and in a shorter time at a wavelength of 365 nm and low irradiance (Figure 4a). The manufacturer's information shows that this type of photoinitiator does not absorb radiation at this wavelength; their λ_{max} is approximately 243 and 330 nm (Table 1). This may be due to the presence of P-telogen in the system. The molar concentration of DMPh is higher than that of the photoinitiator. There may have been a shift in the absorbance of the HAP + DMPh photoinitiating system towards longer wavelengths. In turn, the tested photoinitiators from the APO group or their blends showed the maximum absorption at approximately 370 nm. Hence, the conclusion is that they are better suited to the source of UV radiation. Additionally, they can be used in formulations containing monomers that are strong triplet quenchers, such as styrene. Regardless of the UV range and UV irradiance, in each tested exposure variant, the highest reaction rates were achieved by systems with O819. The only exception was the system in which the UV irradiance was high and the UV range was wide (Figure 4c), whereby the sample with O184 achieved the highest R_p . Nevertheless, this was due to the molar concentration of this photoinitiator being the highest. An additional feature of O819 is the generation of four radicals per photoinitiator molecule. A trimethylbenzoyl radical and trimethylbenzoylphosphinyl radical are formed from the primary scission, both of which are active. The latter radical can undergo further scission, producing a second trimethylbenzoyl radical and a phosphinyl radical, making them very fast and efficient photoinitiators. This is also confirmed by the photoinitiation index results shown in Figure 5a.



Figure 5. Photoinitiation indices for the varnish compositions depending on PIs and UV curing conditions: (a) $I_0 = 90 \text{ mW/cm}^2$, (b) $I_0 = 90 \text{ mW/cm}^2$ or 500 mW/cm^2 .

Interestingly, in the case of all initiating systems used in the process (PI + DMPh), regardless of the type of photoinitiator and at the same low value of I_o (90 mW/cm²), the I_p values were higher when irradiated at 365 nm than in a wide UV range. The I_p increased

significantly with increasing I₀ (500 mW/cm², Figure 5b). Among acylphosphine oxides, the initiation efficiency was as follows: O819 < OTPO < OTPOL. This is consistent with the literature data. However, among the APO blends, in a wide UV range and regardless of the UV irradiance, the initiation efficiencies with O2100 (a mixture of two acylphosphine oxides) and BL750 (a mixture of three oxides) were similar. At 365 nm, O2100 performed better. The kinetic studies of the photopolymerization/phototelomerization processes of the coating composition clearly indicate the higher reactivity of systems with APOs (especially O819) than HAPs. However, APO blends give worse results than single APOs.

3.2. Comparison of UV LEDs and Medium-Pressure Mercury Lamp Used to Cure Coatings

As mentioned above, in the present study, the influence of the UV radiation type in the photocrosslinking process on the hardness of the coatings was tested. UV LEDs (365 nm) or a medium-pressure mercury lamp that emitted UV-ABC radiation (200–420 nm) were used. The effectiveness of the photocrosslinking process was checked using the same UV dose for UV light sources (6 J/cm²). The UV dose (J/cm²) is the total UV energy applied on the coating surface and is released from the lamps during exposure. The dependence of the varnish hardness on the type of photoinitiator and the type of UV-radiating source is shown in Figure 6. Hardness testing was carried out 2 and 7 days after irradiation. Although it is generally believed that radical photopolymerization (as in this case) ends when the light source is switched off, in fact, only the generation of radicals ends, and the radicals that have already formed, in the form of macroradicals, can also participate in the crosslinking process in the dark.



Figure 6. Hardness of the UV-cured varnish coatings cured using UV LEDs or medium-pressure mercury lamp (UV dose of 6 J/cm^2) and tested after 2 (**a**) and 7 (**b**) days.

This can be seen by comparing the varnish hardness results after 2 and 7 days (Figure 6a,b). The latter are higher. The hardness values of the coatings depend mainly on the density of the polymer network. In the studies described here, no multifunctional crosslinking monomer (e.g., PETIA) was used at the photocrosslinking stage to increase the density of the polymer network and improve the hardness of the coatings. This action was intentional. Therefore, the obtained hardened coatings were characterized by relatively low hardness after two days (from approximately 30 to 50 a.u.). The V-O184, V- OTPOL, and V-BL750 coatings were characterized by the highest hardness values, but, in the case of V-184, exposed to the UV-ABC lamp, higher hardness was achieved (52 a.u.) than when using UV LEDs (39 a.u.). In the case of V-TPOL, the hardness values were similar regardless of the radiation source (48–51 a.u.), and the V-BL750 coating was much harder after crosslinking with a UV LED lamp than with UV-ABC (53 and 28 a.u., respectively). Although, after

7 days after exposure, an increase in hardness was observed for each coating, V-184 and V-TPOL were harder after exposure to a UV-ABC lamp (approximately 74 a.u.), as well as V-BL750 after exposure to UV LEDs. The results were slightly different for these three coatings, but, in each case, the FTIR tests revealed the disappearance of bands characteristic of double bonds (Figure 7).



Figure 7. FTIR spectra for the varnish compositions (before UV curing) and for UV-cured varnish coatings 7 days after UV curing process using UV LEDs or a UV medium-pressure mercury lamp (UV dose of 6 J/cm^2): (a) V-184, (b) V-TPOL, (c) V-BL750.

The conversion of double bonds seven days after exposure depending on the type of UV radiation source and the type of photoinitiator is shown in Figure 8. The DC values

were higher than 94%. The highest results (ca. 98%) were obtained in the case of coatings with HAP photoinitiators, because PIs that have strong absorption in the short-wave UV range give good surface curing. Interestingly, even after crosslinking using a UV LED lamp, the DC for these samples (V-127 and V-184) was the highest (similar to V-TPOL, 97%).



Figure 8. Conversion of double bonds ($DC_{C=C}$) for the UV-cured varnish coatings (6 J/cm²).

3.3. Comparison of Different UV Doses

The above studies showed that even low-energy UV radiation emitted from the LED lamp at 365 nm caused the hardening of the coatings. The best results were obtained for the V-TPOL and V-BL750 systems. It should also be mentioned that no oxygen inhibition effect was observed even with the use of APOs. It is known from the literature that APOs give excellent depth curing but relatively poor surface curing, since the phosphinyl radicals are very sensitive to oxygen. In this study, an organophosphate compound, i.e., DMPh, was also present in the photoreactive coating composition. DMPh is composed of di-esters of phosphorous acid. As shown by NMR studies, DMPh is a weak chain transfer agent (weak telogen) because it is incorporated at only 30% into the oligomer structure. However, it is known from the literature that phosphoric acid(III) esters are good antioxidants and may react with peroxygen radicals [35]. For this reason, even at a low UV dose and low UV irradiance (90 mW/cm²), no oxygen inhibition phenomenon was observed (the coatings were dry). This was also confirmed by FTIR tests (high DC values). In the next step, the hardness results of coatings cured with a UV LED lamp were compared, but at a higher UV dose (30 J/cm²). The results are presented in Figure 9. Moreover, the influence of the aging time of the prepared coatings was analyzed.

As can be seen, the hardness values of the coatings increased by almost twice as they aged from 2 to 35 days—for example, from 50 a.u. for V-TPOL and up to 90 a.u. V-BL750. When a low dose of UV LED at 365 nm was applied, better hardness results were achieved each time by V-TPOL. On the other hand, the photoinitiator BL750 proved to be better at higher UV doses (30 J/cm^2), as the V-BL750 coating had already achieved the desired hardness value of 80 a.u. after 14 days of aging. However, the lowest hardness values were noted for varnishes with O184. FTIR studies showed the almost complete disappearance of the 812 cm⁻¹ and 1635 cm⁻¹ characteristic bands in the prepared coatings (Figure 10).







Figure 10. Cont.



Figure 10. FTIR spectra for the varnish compositions (before UV curing) and for UV-cured varnish coatings 35 days after UV curing process using UV LEDs or a UV medium-pressure mercury lamp (UV dose of 6 or 30 J/cm²): (a) V-184, (b) V-TPOL, (c) V-BL750.

The conversion of double bonds in varnishes V-184, V-TPOL, and V-BL750 after aging is shown in Figure 11. All DC values were increased over time. In addition, in the systems with O184 and OTPOL, a higher UV LED dose caused the greater conversion of C=C bonds (approximately 0.5%).



Figure 11. Conversion of double bonds (C=C bonds) in coatings: V-184, V-TPOL, and V-BL750 (tests were performed 7, 14 and 35 days after the UV curing process using UV LEDs with a UV dose of 6 J/cm^2 or 30 J/cm^2).

4. Conclusions

In this study, the UV curing process of coatings based on (meth)acrylic/styrene telomers with terminal P-atoms (prepared via a UV phototelomerization process) was analyzed. The influence of the type of photoinitiator (HAPs, APOs, or APO blends), as well as the UV radiation source (medium-pressure mercury lamp or UV LEDs), was tested. The UV curing kinetics and hardness of the varnishes were presented. The main conclusions are as follows:

- Photopolymerization/phototelomerization processes during the UV curing of the coating formulations occurred much faster at high UV irradiance (conditions such as the UV curing process realized with a UV-ABC-type medium-pressure mercury lamp). Moreover, the kinetics of these processes indicated the higher reactivity of systems with APOs than HAPs (regardless of the incident light intensity).
- Among acylphosphine oxides, the initiation efficiency is as follows: O819 < OTPO < OTPOL.
- The kinetic results did not correspond with the hardness values of the coatings. The APO systems with the lowest reactivity (V-TPOL) allowed the preparation of the hardest varnishes.
- The formulations with TPOL were suitable both for curing with UV LED at 365 nm and a UV-ABC-type medium-pressure mercury lamp (hardness values were similar).
- The presence of phosphoric acid diesters, e.g., dimethyl phosphite, has a beneficial effect on the photocrosslinking process at a low UV dose and low UV irradiation, because DMPh acts as an antioxidant, which allows for effective crosslinking even when using APO-type photoinitiators.

Coating compositions based on phosphorus (meth)acrylate telomeres and containing free monomers and dimethyl phosphite (as a telogen and antioxidant) can be used even without the use of a crosslinking monomer to produce relatively hard varnishes. It has been shown that the UV crosslinking process is possible using low-energy radiation sources and photoinitiators from the group of acylphosphine oxides, without the effect of oxygen inhibition in the surface layer. Due to the presence of hydroxyl groups in the coating (derived from 2-hydroxyethyl acrylate), they are characterized by good adhesion to glass and metal (as shown in [32]). Additionally, a positive influence is exerted by P=O groups (from telogen), which is related to the formation of hydrogen bonds between the P=O groups and the HO-Si groups from the surface.

Author Contributions: Conceptualization, A.K. (Agata Kraśkiewicz) and A.K. (Agnieszka Kowalczyk); methodology, A.K. (Agnieszka Kowalczyk) and A.K. (Agata Kraśkiewicz); investigation, A.K. (Agata Kraśkiewicz) and A.K. (Agnieszka Kowalczyk); writing—original draft preparation, A.K. (Agnieszka Kowalczyk) and A.K. (Agata Kraśkiewicz); writing—review and editing, A.K. (Agnieszka Kowalczyk); visualization, A.K. (Agata Kraśkiewicz) and A.K. (Agnieszka Kowalczyk); supervision, A.K. (Agnieszka Kowalczyk). All authors have read and agreed to the published version of the manuscript.

Funding: The APC was supported by the Rector of the West Pomeranian University of Technology in Szczecin for PhD students of the Doctoral School, grant number: ZUT/5/2023.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The data presented in this study are available on request from the corresponding author.

Conflicts of Interest: The authors declare no conflict of interest.

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Article The Impact of Topological States on the Thermoelectric Performance of p- and n-Type Sb₂Te₃/Bi₂Se₃-Multiwalled Carbon Nanotubes Heterostructured Networks

Jana Andzane¹, Krisjanis Buks^{1,2}, Elmars Spalva², Andrei Felsharuk¹ and Donats Erts^{1,3,*}

- ¹ Institute of Chemical Physics, University of Latvia, Raina Blvd. 19, LV-1586 Riga, Latvia
- ² 3D Strong Ltd., Instituta Str. 36-17, LV-2130 Ulbroka, Latvia
- ³ Faculty of Chemistry, University of Latvia, 1 Jelgavas Str., LV-1004 Riga, Latvia

Correspondence: donats.erts@lu.lv

Abstract: The resistance and magnetoresistance of flexible thermoelectric p-type Sb₂Te₃-MWCNT, p-type Bi₂Se₃-MWCNT, and n-type Bi₂Se₃-MWCNT heterostructures were studied in the temperature range from 2 K to 300 K to reveal the conductance mechanisms governing the thermoelectric properties of these heterostructured networks. It was found that the conductance in heterostructured networks at different temperatures is governed by different processes and components of the networks. This effect was found to be related to the growth mechanisms of the Sb₂Te₃ and Bi₂Se₃ nanostructures on the MWCNT networks. At near-room temperatures, the Sb₂Te₃ and Bi₂Se₃ nanostructures were found to have the dominant contribution to the total conductance of the p-type Sb₂Te₃-MWCNT and n-type Bi₂Se₃-MWCNT networks. In turn, the conduction of p-type Bi₂Se₃-MWCNT heterostructured networks in a full temperature range and p-type Sb₂Te₃ and Bi₂Se₃ nanostructures, heterostructured networks at temperatures below 30 K was governed by the MWCNTs; however, with the contribution from 2D topological states of Sb₂Te₃ and Bi₂Se₃ nanostructures, these were manifested by the weak antilocalization effect (WAL) cusps observed at temperatures below 5–10 K for all heterostructured networks considered in this work.

Keywords: topological insulator-carbon nanotube interface; heterostructured network; thermoelectric film; domestic waste heat conversion; magnetoresistance; bismuth and antimony chalcogenide

1. Introduction

In recent years, the study of nanostructured thermoelectric (TE) materials has become an emerging topic due to the increasing demand for energy-efficient processes and minimizing heat loss. TE material-based devices can transform waste heat into useful electrical energy and be used for thermal sensing [1]. The efficiency of TE materials is judged by the dimensionless figure of merit ZT, which is defined as $S^2 \cdot \sigma \cdot T \cdot \kappa^{-1}$, where S is the Seebeck coefficient of TE material, σ and κ are its electrical and thermal conductivities, respectively, and T is the absolute temperature. To increase the ZT of the material, it is necessary to increase σ and decrease κ ; however, according to the Wiedemann–Franz law, the σ/κ ratio in bulk TE materials is restricted [2]. Bismuth and antimony chalcogenides (Bi₂Se₃, Bi₂Te₃, Sb₂Te₃, etc.) are widely known layered thermoelectric materials belonging to a class of 3D topological insulators (TI) [3-7]. Recently, it was predicted theoretically that downsizing these materials to the thickness of a few nm may form a hybridization gap between the top and bottom surface states of the material, resulting in the disengagement of σ and κ and a potentially significant increase in the existing ZT of the material [8,9]. At the same time, other theoretical works demonstrate that the parallel contribution of bulk and surface channels tend to cancel each other out, and the improvement of ZT in TIs with thicknesses below 10 nm is insignificant [10]. The experimental assay of these theoretical predictions performed for ultrathin Bi₂Se₃ and Sb₂Te₃ thin films were grown using the molecular beam

Citation: Andzane, J.; Buks, K.; Spalva, E.; Felsharuk, A.; Erts, D. The Impact of Topological States on the Thermoelectric Performance of pand n-Type Sb₂Te₃/Bi₂Se₃-Multiwalled Carbon Nanotubes Heterostructured Networks. *Coatings* **2023**, *13*, 2082. https://doi.org/ 10.3390/coatings13122082

Academic Editors: Jose Maria De Teresa, Ricardo Lopez Anton and Sion Federico Olive Méndez

Received: 16 November 2023 Revised: 8 December 2023 Accepted: 12 December 2023 Published: 14 December 2023



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epitaxy (MBE) [10] or physical vapor deposition (PVD) [11] methods, yet did not show any significant improvement from the bulk values of ZT, which was attributed to the opposite contributions of the bulk and surface states of these materials. However, ultrathin (5-15 nm) the Bi_2Se_3 and (5–7 nm) Sb_2Te_3 films deposited by the PVD method showed thermoelectric properties comparable with thick MBE-grown thin films, presumably due to the quantum confinement effects originating from the downsizing and possible gapping of the topological surface states, and demonstrated their significant potential for their applications in TE generators (TEG) [11]. However, the main drawback to the application of Bi_2Se_3 and Sb₂Te₃ ultrathin films in TEGs is their fragility and the necessity to use solid substrates, which have relatively high thermal conductance. Recently, it was demonstrated by different research groups that combining bismuth and antimony chalcogenide nanostructures with carbon nanotubes (CNT) via the direct deposition of inorganic nanostructures on the CNT network via sputtering or PVD methods results in the formation of heterostructures which exhibit Seebeck coefficients comparable with that of bulk inorganic TE materials [12-16] and ZTs reaching 0.89 for some heterostructures, such as, for instance, Bi₂Te₃-CNT hybrid nanostructure scaffolds [12]. This high ZT value was attributed to the combination of the high electrical and low thermal conductivity of CNT networks [17] and the good room temperature thermoelectric properties of Bi₂Se₃, Bi₂Te₃ and Sb₂Te₃ [18,19]. The possibility of encapsulating such TI-CNT heterostructured networks in the non-conductive polymer without the significant degradation of thermoelectric properties and their high flexibility and mechanical and electrical stability under repetitive bending makes them attractive for use in wearable thermoelectric devices and other flexible electronic applications [20–22]. It was also shown that the PVD deposition of Bi₂Se₃ nanostructures on the MWCNT surface results in the formation of an up to 5 nm thin single-crystalline Bi₂Se₃ layer around the MWCNT, followed by the formation of free-standing Bi₂Se₃ nanoplates [16]. Thus, the good thermoelectric performance of bismuth chalcogenide-CNT heterostructures may also be the result of the contribution of topological surface states of Bi2Te3 or Bi2Se3 as was theoretically predicted. Potentially, dominating conductance mechanisms and the possible contribution of topological surface states to the properties of TI-CNT heterostructures may be revealed by analyzing the magnetoresistance measurements of the heterostructures. In recent years, topological insulator nanostructures have been found to exhibit magnetoresistance properties characterized by weak anti-localization (WAL) effects at temperatures below 30 K and low magnetic fields, which originate from the surface states of these materials [23–27]. In turn, the magnetoresistance of CNTs at low temperatures and low magnetic fields reveals the presence of weak localization (WL) effects [28-30]. The observation of WL and WAL effects in TI-CNT heterostructures, originating from the interface or interplay of the heterostructure components, may shed light on the dominating charge transfer processes occurring in these systems at different temperatures. For example, the presence of the WAL effect in Bi₂Se₃/Sb₂Te₃-MWCNT heterostructures indicates the suppression of bulk states due to the processes occurring at the interface between the TI and MWCNT and domination of the surface states in the TI material deposited on the MWCNTs. The hybridization of these surface states without compensating the contribution of bulk states could lead to a significant increase in the existing ZT of the bulk TI material [8,9]. This is interesting as thermoelectrics could open the path for the further employment of the hybridization effect of the topological surface states and for the improvement of properties of thermoelectric materials by combining them with CNTs, as well as many low-temperature spintronic applications [31,32], including magnetic sensors and memory devices [33,34], where magnetoresistance properties are crucial. However, to our knowledge, the systematic investigation of magnetoresistance in Bi_2Se_3/Sb_2Te_3 -CNT heterostructures in the temperature range from 2 K to room temperature has not yet been performed.

In this work, the temperature dependencies of the resistance and magnetoresistance of p-type Sb₂Te₃-multiwalled carbon nanotubes (MWCNT) and p- and n-type Bi₂Se₃-MWCNT heterostructures were studied and analyzed to reveal the conductance mechanisms in these heterostructured networks. The results of this work provide insight into the potential use of

these heterostructured nanostructures in both thermoelectric and magnetoresistance-based applications.

2. Materials and Methods

2.1. Synthesis of MWCNTs

MWCNTs were synthesized using the chemical vapor deposition (CVD) method in a horizontal gas flow reactor. In this synthesis, ferrocene $Fe(C_5H_5)_2$ was used as a source for catalytic Fe nanoparticles. $Fe(C_5H_5)_2$ was dissolved in benzene at a concentration of 2 wt.%, and 100 mL of this solution was used for each synthesis cycle. An aerosol $Fe(C_5H_5)_2$ solution was then sprayed through a dispenser into the synthesis reactor at around 200 °C using argon as the carrier gas at a 20 mm/s flow rate. The total duration of the synthesis was 20 min. After cooling down the synthesis reactor, the MWCNTs were separated from the surface of the quartz tube of the reactor, yielding an MWCNT powder [35].

2.2. Synthesis of Sb₂Te₃/Bi₂Se₃-MWCNT Heterostructures

To obtain the Sb₂Te₃ or Bi₂Se₃ and MWCNT hybrid nanostructures, the MWCNTs' networks were first prepared on 25×25 mm² glass substrates using the spray-coating method—a 0.1 wt.% MWCNT suspension in isopropyl alcohol (IPA) was used for the spraycoating, resulting in MWCNT networks with a mass density of approximately 0.01 mg/cm². Afterwards, Bi₂Se₃ or Sb₂Te₃ nanostructures were deposited on the MWCNT networks using the catalyst-free physical vapor deposition method in a single-zone quartz furnace tube (GCL-1100X; MTI Corp., Richmond, CA, USA) equipped with a vacuum pump and nitrogen gas supply [16,36]. The Bi₂Se₃ or Sb₂Te₃ source material was placed in the center of the hot zone of the furnace at 585 °C, while the glass/MWCNT substrate was placed in the 470–390 °C zone. After this, the quartz furnace tube was flushed with nitrogen for 5 min, pumped down to a base pressure of 400 mTorr, and finally sealed. The synthesis was carried out by heating the quartz tube to a 585 °C temperature at a rate of 13 °C/min and then holding it at 585 °C for 15 min, after which the tube was left to cool naturally. As the tube cooled to 475 °C, it was filled with nitrogen and atmospheric pressure. The reference Sb₂Te₃ and Bi₂Se₃ nanostructured thin films were prepared using the same synthesis method with glass substrates. The thicknesses of the reference thin films were in the range of 200–400 nm. The amount of Bi_2Se_3 nanostructures deposited on the MWCNT networks varied depending on the amount of source material and the deposition duration. The wt.% of MWCNTs in Sb₂Te₃-MWCNT and Bi₂Se₃-MWCNT heterostructured networks was determined by weighing the substrate at each stage of preparation of the hybrid nanostructures (glass, bare MWCNT-coated glass, Sb₂Te₃/Bi₂Se₃-MWCNT coated glass) using an analytical balance (Precisa XR 205SM-DR, Dietikon, Switzerland).

2.3. The Morphology and Chemical Composition of the Samples

The morphology of the samples was characterized using a Hitachi S-4800 fieldemission scanning electron microscope equipped with an energy-dispersive X-ray analyzer (123 eV; Bruker XFlash Quad 5040, Billerica, MA, USA). X-ray photoelectron spectroscopy measurements were carried out using a ThermoFisher ESCALAB Xi+ instrument with a monochromatic Al K α X-ray source. The instrument-binding energy scale was calibrated to give a binding energy of 932.6 eV for the Cu $2p_{3/2}$ line of freshly etched metallic copper. The X-beam size used for the spectra recording was 900 × 10 µm with a pass energy of 20 eV and step size of 0.1 eV.

2.4. Room-Temperature Seebeck Coefficient Measurements

Room temperature Seebeck coefficient measurements were performed under ambient conditions using a laboratory-made device consisting of a Keithley 6430 Sub-Femtoamp remote source meter and an HP34401A digital multimeter; the device was calibrated using Standard Reference Material 3451 for the low-temperature Seebeck coefficient (NIST). For the Seebeck coefficient measurements, a two-part silver conductive epoxy (Agar scientific G3040, Stansted Mountfitchet, UK) was used to fabricate electrodes and to bond copper wires to each side of the hybrid network.

2.5. Magnetoresistance Measurements in the Temperature Range 2–300 K

Magnetoresistance (MR) is defined as MR = $(\rho(B) - \rho(0))/(\rho(0))$, where B is the magnetic field strength and $\rho(0)$ and $\rho(B)$ are the MWCNT film resistivities in the presence and absence of the magnetic field, respectively. For the determination of magnetoresistance, the resistances of the MWCNT networks were measured in a classic Hall bar configuration using the physical property measurement system (PPMS DynaCool-9T, Quantum Design, San Diego, CA, USA) at temperature and magnetic field strength in the range of 2 to 300 K and -9 T to +9 T, respectively. The samples were $10 \text{ mm} \times 10 \text{ mm}$ in size; electrodes (70 nm Gold/5 nm Titanium) were applied using the thermal evaporation method (SIDRABE SAF EM sputtering vacuum system, Riga, Latvia). For the resistivity calculation, the thicknesses of the samples were measured using a profilometer Veeco Dektak 150.

3. Results and Discussion

Sb₂Te₃-MWCNT (with 6.5 wt.% of MWCNTs) and Bi₂Se₃-MWCNT (with 3 and 7.5 wt.% of MWCNTs) heterostructures were synthesized via the physical vapor deposition of Sb₂Te₃ or Bi₂Se₃ on pre-fabricated MWCNT networks, as shown in the schematics in Figure 1 and described elsewhere [16].



Figure 1. Schematics of the fabrication process of Bi₂Se₃/Sb₂Te₃-MWCNT heterostructured networks.

Deposited on the MWCNT network (Figure 2a), Bi_2Se_3 (Figure 2b), and Sb_2Te_3 (Figure 2c), nanostructures were represented mainly by randomly oriented nanoplate-like structures with thicknesses ~50–150 nm and ~300 nm, respectively.

While graphene substrates promote the epitaxial growth of Bi₂Se₃ and Sb₂Te₃ nanostructures due to the low lattice mismatch between graphene and Bi₂Se₃ or Sb₂Te₃ [37,38], a fundamental difference between the Bi2Se3-MWCNT and Sb2Te3-MWCNT heterostructures is found in the growth mechanism of the Bi₂Se₃ and Sb₂Te₃ nanostructures on the surfaces of curved nanotubes; while Bi₂Se₃ form shells around the individual MWCNTs, subsequently forming 15–30 nm thin nanoplates, the Sb₂Te₃ forms clusters of several hundred nanometers in size on energetically favorable locations, such as the junctions of nanotubes, without forming core-shell structures with the nanotubes, as described in detail in our previous work [16]. The chemical compositions of the synthesized MWCNT Sb_2Te_3 and Bi₂Se₃ nanostructures determined using EDX were 41 ± 3 at% Sb and 59 ± 3 at% Te and 42 ± 2 at% Bi and 58 ± 3 at% Se, respectively, which corresponds to stoichiometric Sb₂Te₃ and Bi₂Se₃. The chemical composition was confirmed using the XPS spectra recorded for the Bi₂Se₃ and Sb₂Te₃ nanostructured layers coating the MWCNTs in the Bi₂Se₃-MWCNT and Sb₂Te₃-MWCNT heterostructures. The deconvoluted high-resolution Bi 4f and Se 3d XPS spectra of the Bi₂Se₃ nanostructures revealed peaks located at 158.2 eV (Figure 2d), 53.8 eV, and 54.6 eV (Figure 2e), corresponding to Bi $4f_{7/2}$, Se $3d_{5/2}$ and Se $3d_{3/2}$, respectively, in the Bi₂Se₃ compound. The lower intensity peaks located at 158.9 eV (Figure 2d) and 54.8 eV (Figure 2e) correspond to the oxidized Bi₂Se₃, which is related to the presence of native oxide layer-coating Bi₂Se₃ nanostructures. The Bi:Se at.% profile recorded during the etching of the surface of Bi₂Se₃ nanostructures confirmed their chemical composition as 42 \pm 2 at% Bi and 58 \pm 3 at% Se (Figure 2f). Peaks located at 530.2 eV (Figure 2g) and 573.6 eV (Figure 2h) correspond to Sb 3d_{5/2} and Te 3d_{5/2}, respectively, in the Sb₂Te₃ compound. In turn, the peaks located at 531 eV (Figure 2g) and 576.8 eV (Figure 2h) correspond to the oxidized Sb₂Te₃. A relatively high intensity of these peaks is related to the susceptibility of the Sb₂Te₃ compound to rapid oxidation in air [39]. In addition, a peak located at 531.5 eV (Figure 2g) corresponds to the O1s signal, presumably originating from the hydroxyls of water adsorbed on the oxide layer in ambient conditions [40]. The Sb:Te at.% profile recorded during the etching of the surface of Sb₂Te₃ nanostructures confirmed their chemical composition at 41 \pm 3 at% Bi and 58 \pm 4 at% Te (Figure 2i) after the native oxide layer-coating Sb₂Te₃ nanostructures was etched off.



Figure 2. SEM images of (**a**) the bare MWCNT network, (**b**) the Bi₂Se₃-MWCNT heterostructured network, (**c**) Sb₂Te₃-MWCNT heterostructured network; (**d**,*e*,*g*,**h**) representative deconvoluted X-ray photoelectron spectroscopy (XPS) spectra of (**d**,*e*) Bi₂Se₃, and (**g**,**h**) Sb₂Te₃ nanostructured components of heterostructured networks (red and black curves represent respectively experimental data and fitting to the experimental data); and the (**f**,**i**) chemical composition of (**h**) Bi₂Se₃ and (**i**) Sb₂Te₃ nanostructures vs. etching time, recorded using XPS.

Based on previous research [16], MWCNT 6.5 wt.% in the Sb₂Te₃-MWCNT heterostructures was selected to obtain a Seebeck coefficient as high as possible while retaining the flexibility of the Sb₂Te₃-MWCNT network. In turn, in the case of Bi₂Se₃-MWCNT structures, MWCNT wt.% was chosen to obtain both negative and positive Seebeck coefficient values (Table 1). In the case of the deposition of Bi₂Se₃ (naturally n-type) on MWCNTs (naturally p-type), both components contributed to the Seebeck coefficient, tending to cancel each other. Thus, the Bi₂Se₃-MWCNT heterostructured networks with resulting n-type conductance can be obtained only at a low MWCNT wt.% in the heterostructures. In this case, the contribution of the established MWCNT Bi₂Se₃ network is dominant. The MWCNT wt.%related transition from n-type to p-type conductance in these heterostructures is relatively rapid and occurs around the MWCNT content of 7–10 wt.% when the contribution of the MWCNTs to the Seebeck coefficient exceeds the contribution of Bi₂Se₃ [16].

Table 1. Seebeck coefficient values of different samples studied in this work.

Sample	Seebeck Coefficient, $\mu V \cdot K^{-1}$	
Bare MWCNT network	$+16 \pm 5$	
Sb ₂ Te ₃ -MWCNT network with MWCNT content 6.5 wt.%	$+74\pm7$	
Bi ₂ Se ₃ -MWCNT network with MWCNT content 7.5 wt.%	$+11 \pm 3$	
Bi ₂ Se ₃ -MWCNT network with MWCNT content three wt.%	-52 ± 5	
Sb_2Te_3 thin film	$+85\pm8$	
Bi ₂ Se ₃ thin film	-100 ± 11	

It can be seen from Table 1 that the bare MWCNT network had a p-type conductance and a Seebeck coefficient of ~+16 μ V·K⁻¹, which is a typical value for undoped MWCNTs [41]. Nanostructured Bi₂Se₃ and Sb₂Te₃ thin films, synthesized via the catalystfree physical vapor deposition process, had Seebeck coefficients of ~-100 μ V·K⁻¹ and ~+85 μ V·K⁻¹, respectively, which are the values expected for these materials [16,36], and also indicate the type of conductance of these materials. The Seebeck coefficient value of ~+74 μ V·K⁻¹ obtained for Sb₂Te₃-MWCNT also correlates with previously reported data [16,42]. It indicates the dominant contribution of Sb₂Te₃ nanostructures to the total conductance of the Sb₂Te₃-MWCNT heterostructured network at room temperature. By contrast, Bi₂Se₃-MWCNT heterostructured networks showed Seebeck coefficients of ~+11 μ V·K⁻¹ for the network containing 7.5 wt.% of MWCNTs (referred to as p-type Bi₂Se₃-MWCNTs (referred to as n-type Bi₂Se₃-MWCNTs further in the text) and ~-52 μ V·K⁻¹ for the network containing three wt.% of MWCNTs (referred to as n-type Bi₂Se₃-MWCNTs further in the text). These data indicate the presence of competing conduction mechanisms in the Bi₂Se₃-MWCNT heterostructures, both contributing to the total conductance.

To reveal the mechanisms governing the conduction in Sb₂Te₃-MWCNT and Bi₂Se₃-MWCNT-heterostructured networks, the resistance R and magnetoresistance MR of these samples were studied in the temperature region of 2–300 K. R(T) dependencies of bare MWCNT networks (Figure 3a) and reference nanostructured Sb₂Te₃ and Bi₂Se₃ thin films (Figure 3b,c) were shown to be typical for these materials' behavior [35,43–45]. The R(T) curve for the bare MWCNT network showed semiconductor behavior, where a monotonous incremental increase in the resistance with the decrease in the temperature from 300 K to ~30 K was followed by a rapid increase in resistance at temperatures below 30 K (Figure 3a).



Figure 3. Temperature dependencies of resistance R of (**a**) the bare MWCNT network; (**b**) Sb₂Te₃ thin film; (**c**) Bi₂Se₃ thin film; (**d**) Sb₂Te₃-MWCNT heterostructured network; (**e**) p-type Bi₂Se₃-MWCNT heterostructured network; (**f**) and n-type Bi₂Se₃-MWCNT heterostructured network. Insets: ln(R) vs. $T^{1/4}$ plots (dashed curves represent fitting to the experimental data).

In the temperature region, 5–300 K, the R(T) curve of the bare MWCNT network (Figure 2a, inset) fitted well to the 3D Mott variable-range hopping (VRH) model for disordered systems [46–49], where conductance can be described by charge carrier hopping through localized states near the Fermi level and follows the formula $R = R_0 exp((T_0/T)^{1/4})$, where R_0 is a constant of proportionality representing the resistance of the sample at room temperature, and T_0 is Mott's characteristic temperature which is related to the energy required for the hopping of charge carriers and is determined as $T_0 = \beta/(k_B g(\mu) \alpha^3)$, where $\beta = 21$, k_B is the Boltzmann's constant, $g(\mu)$ is the density of states near the Fermi level and α is the localization length. At temperatures below 5 K, a deviation from Mott's law was observed due to Coulomb interactions between the localized electrons, which are not considered in Mott's model. In turn, as shown in Figure 3b,c, the R(T) curves of the nanostructured Sb₂Te₃ and Bi₂Se₃ thin films showed typical metallic behavior, expressed as a gradual decrease in the resistance with the decrease in temperature, which is in line with previous reports on the thin films of these materials [43,44]. However, the R(T) curve of the Sb₂Te₃-MWCNT heterostructured network showed a decrease in the resistance when the temperature decreased from 300 K to ~150 K, followed by its upturn at temperatures below 150 K with a rapid increase at temperatures below 30 K (Figure 3d). The U-turn shape of the R(T) curve of the Sb₂Te₃-MWCNT network indicates the temperature-dependent contribution of different mechanisms to the total conductance of this network. At temperatures between 5 and 150 K, the R(T) curve fits well with Mott's 3D VRH model (Figure 3d, inset), which indicates the domination of the hopping mechanism of conduction, which is typical for disordered CNT networks. At temperatures below 5 K, similar to that observed in the case of the bare MWCNT network, deviations from Mott's law, indicating Coulomb interactions between the localized electrons, were observed (Figure 3d, inset). However, the total resistance of the Sb₂Te₃-MWCNT heterostructured network was approximate. An order of magnitude smaller than the resistance of the bare MWCNT network (Figure 3a) was comparable with the resistance values of the Sb₂Te₃ thin film (Figure 3b). Presumably, the decreased resistance in the temperature region 2-150 K was because of the effective charge transfer that occurred at the Sb₂Te₃-MWCNT interface and/or the increased mobility of the charge carriers due to the reduced Sb_2Te_3 interface barriers [50,51]. In the temperature region above 150 K, the Sb₂Te₃-MWCNT networks exhibit metallic behavior (Figure 3d), indicating the dominating contribution of interconnected Sb₂Te₃ nanostructures to the total conductance of the sample. The domination and the contribution of interconnected Sb₂Te₃ nanostructures to the total conductance of the Sb₂Te₃-MWCNT network is in line with the Seebeck coefficient of this network and is comparable with the Seebeck coefficient of the reference nanostructured Sb₂Te₃ thin film (74 $\mu V \cdot K^{-1}$ vs. 85 $\mu V \cdot K^{-1}$, Table 1). In addition, a significant difference was observed between the slopes of $\ln(R)$ vs. $T^{-1/4}$ curves of the bare MWCNT network ($\sim 2.13 \cdot T^{-1/4}$, Figure 3a, inset) and Sb₂Te₃-MWCNT ($\sim 0.82 \cdot T^{-1/4}$, Figure 3d, inset). Considering that the slopes of the ln(R) vs. $T^{-1/4}$ are related to Mott's characteristic temperature T_0 , a possible reason for the lower slope of the ln(R) vs. $T^{-1/4}$ curve of Sb₂Te₃-MWCNT heterostructured networks in comparison with the slope of the bare MWCNT network is the increase in the localization length, and consequently, the increase in the charge carrier hopping distance and mobility [48,49].

In contrast with Sb₂Te₃-MWCNT, the R(T) curves of p-type and n-type Bi₂Se₃-MWCNT heterostructured networks (Figure 3e,f) showed a semiconductor behavior similar to bare MWCNT networks (Figure 3a). The R(T) curve of the p-type Bi₂Se₃-MWCNT network showed an incremental increase in the resistance with the decrease in temperature from 300 K down to ~30 K, followed by the rapid increase in the resistance at temperatures below 30 K (Figure 3e). At temperatures between 3 and 150 K, the R(T) curve fit Mott's 3D VRH model (Figure 3e, inset), which indicated the domination of the hopping mechanism of conduction similarly to disordered CNT networks [35,52-54]. The resistance values shown by the p-type Bi₂Se₃-MWCNT network were slightly lower in comparison with that of bare MWCNT networks, which could be related to the increase in localization length of the charge carriers due to the reduced potential barriers at MWCNT/Bi₂Se₃ interfaces similarly to the case of the Sb₂Te₃-MWCNT heterostructured network. This is supported by the lower value of the slope of the ln(R) vs. $T^{-1/4}$ curve of the p-type Bi₂Se₃-MWCNT network (Figure 3e) in comparison with that of the bare MWCNT network ($1.62 \cdot T^{-1/4}$ vs. $2.13 \cdot T^{-1/4}$). In addition, there was a lower slope of the R(T) curve for the p-type Bi₂Se₃-MWCNT heterostructured network in the temperature range 100–300 K (~-0.88 T, Figure 3e) in comparison with that of the bare MWCNT network (~ -1.16 ·T, Figure 3a), which may indicate the contribution of the metallic conductance of interconnected Bi₂Se₃ nanostructures to the total conductance of the p-type Bi₂Se₃-MWCNT network. This presumption is supported by the Seebeck coefficient values of the p-type Bi₂Se₃-MWCNT heterostructured network, which are lower by ~30% than the Seebeck coefficient values of bare MWCNT networks (Table 1). However, the positive values of the Seebeck coefficient or p-type Bi₂Se₃-MWCNT networks indicate that the contribution of Bi₂Se₃ to the total conductance, in this case, is not dominating. In turn, R(T) curve of the n-type Bi₂Se₃-MWCNT heterostructured network showed a nonlinear incremental increase in R with a temperature decrease from 300 K down to 100 K (Figure 3f), indicating the presence of two competing temperature-dependent mechanisms of conductance, followed by the rapid increase in R in the temperature region below 30 K (Figure 3f), which was similar to that shown by the bare MWCNT network (Figure 3a). Noticeable deviations in the R(T) curve from Mott's 3D VRH model in the temperature region above 30 K (Figure 3f, inset) suggest the contribution of the metallic conductance mechanism and phonon-assisted conduction processes to the total conductance of the n-type Bi₂Se₃-MWCNT heterostructured network. The slope of the ln(R) vs. $T^{-1/4}$ curve is lower in comparison with that of p-type Bi₂Se₃-MWCNT heterostructured networks (~ $1.05 \cdot T^{-1/4}$ vs. $1.62 \cdot T^{-1/4}$, Figure 3e,f), which may point to the further increase in the localization length in comparison with p-type Bi₂Se₃-MWCNT networks. However, the resistance of the n-type Bi₂Se₃-MWCNT network is

higher than that of the p-type Bi₂Se₃-MWCNT network and comparable with the resistance of the bare MWCNT network. Considering the negative Seebeck coefficient values of the n-type Bi₂Se₃-MWCNT heterostructured networks (\sim -52 μ V·K⁻¹, Table 1), presumably, the dominating conduction path in the case of n-type Bi₂Se₃-MWCNT heterostructured networks is through the thin Bi₂Se₃ layers formed on the surfaces of MWCNTs. As was reported previously, the direct physical vapor deposition of Bi₂Se₃ on the surfaces of MWCNTs resulted in the formation of an up to 5 nm thin Bi₂Se₃ layer around the MWCNT, followed by the growth of free-standing Bi₂Se₃ nanostructures [16]. Presumably, in p-type Bi₂Se₃-MWCNT networks, the contribution of Bi₂Se₃ to the total conductance comes from the interconnected free-standing Bi₂Se₃ nanoplates, while thin Bi₂Se₃ layers grown on the surfaces of MWCNTs do not form a well-interconnected network. However, in the n-type Bi₂Se₃-MWCNT network, the Bi₂Se₃ thin layers formed on the surfaces of MWCNTs may be interconnected. Previously, it has been shown by other research groups that the deposition of Bi₂Se₃ on graphene results in the formation of a separate n-type conductive channel in the Bi₂Se₃-graphene system if the Bi₂Se₃ thickness is <8 nm [55]. In addition, it was shown by our research group that in contrast to the behavior of Bi₂Se₃-nanostructured thin films with thicknesses above 10 nm, showing the metallic type of conductance, Bi₂Se₃ thin films with thicknesses below 6 nm show a semiconductor type of conductance, expressed as an increase in the resistance with a decrease in temperature [11]. In addition, the Seebeck coefficient shown by ~5 nm thin Bi₂Se₃ films was ~-40 μ V·K⁻¹ [11], which is comparable with the Seebeck coefficient shown by the n-type Bi_2Se_3 -MWCNT network (~-52 μ V·K⁻¹, Table 1).

Magnetoresistance measurements confirmed the different mechanisms of the total conductance of Sb₂Te₃-MWCNT and Bi₂Se₃-MWCNT heterostructured networks. The magnetoresistance of bare MWCNT networks was found to be negative in all ranges of magnetic fields and temperatures and to increase with the decrease in temperature, reaching ~-10% at a temperature of 2 K and magnetic field B of \pm 9 T (Figure 4a). Such magnetoresistance behavior is typical for p-type MWCNTs. Generally, it is explained by the relative changes in conductivity due to the effects of weak localization and charge carriers' interaction, which are both proportional to the temperature [35,53].

In contrast, the magnetoresistance of Sb₂Te₃ (Figure 4b) and Bi₂Se₃ (Figure 4c) nanostructured films were found to be positive in all ranges of temperatures and magnetic fields, reaching ~10% for Sb₂Te₃ nanostructured films and ~30% for Bi₂Se₃ nanostructured films at a temperature of 2–30 K and B \pm 9T. Positive magnetoresistance is typical for the Sb₂Te₃ and Bi₂Se₃ with the metallic type of conductance [23,43,56,57]. It is generally explained as caused by the Lorentz force deflecting the charge carriers from the initial path to cyclotron orbiting. Both Sb₂Te₃ and Bi₂Se₃ exhibit B^2 dependence of the magnetoresistance (Figure 4b,c), which is characteristic of the dominating bulk transport [23]. Positive magnetoresistance decreases with the increase in temperature due to the suppression of mobility in the charge carriers because of phonon-assisted charge carrier scattering. No weak antilocalization effect was observed for the Sb₂Te₃ thin film (Figure 4b, inset), presumably due to the significant thickness of the Sb₂Te₃ thin film, resulting in the presence of dominant bulk charge carriers, masking the effects arising from topologically protected surface states. In contrast, despite the B^2 dependence of magnetoresistance, indicating the domination of bulk charge carriers, the Bi2Se3 thin film exhibited a slight WAL at temperatures below 10 K (Figure 4c, inset). Typically, WAL is observed in Bi₂Se₃ thin films with thicknesses of <100 nm [23]. The weak WAL effect in thicker Bi₂Se₃ nanostructured film could be related to the fact that this film is nanostructured and consists of randomly oriented nanoplates [58].



Figure 4. Magnetoresistance at different temperatures of (**a**) the bare MWCNT network; (**b**) Sb_2Te_3 nanostructured thin film; (**c**) Bi_2Se_3 nanostructured thin film; (**d**) the Sb_2Te_3 -MWCNT heterostructured network; (**e**) p-type Bi_2Se_3 -MWCNT heterostructured network; (**f**) and n-type $Bi_$

Despite both components of Sb₂Te₃-MWCNT heterostructured networks being naturally p-type, their magnetoresistance (Figure 4d) indicates the presence of different competing temperature-dependent mechanisms of conductance observed previously in the R vs. T behavior of the samples. At temperatures above 75 K, the magnetoresistance of the Sb₂Te₃-MWCNT heterostructured networks is positive and follows the tendency of the magnetoresistance of the Sb₂Te₃ thin film (Figure 4b), which most likely points to the dominant contribution of Sb₂Te₃ nanostructures to the conductance of the sample. However, the magnitude of the positive magnetoresistance of the MWCNT-Sb₂Te₃ hybrid network is by an order of magnitude smaller in comparison with that of the Sb₂Te₃ thin film, and presumably due to the competing effect of the negative magnetoresistance of MWCNTs. At temperatures of 30 K and below, the magnetoresistance becomes negative and increases with the temperature decrease at low magnetic fields. However, it exhibits a U-turn to positive values at high magnetic fields (Figure 4d). Presumably, the dominant contribution to the magnetoresistance comes from the MWCNTs at low magnetic fields and low temperatures. However, at higher magnetic fields, the contribution of the positive magnetoresistance of the Sb_2Te_3 network, arising from the impact of the Lorentz force, becomes significant and results in a U-turn in the total magnetoresistance (Figure 4d). The absolute values of negative magnetoresistance of Sb₂Te₃-MWCNT networks are also by an approximate order of magnitude more minor in comparison with the magnetoresistance of bare MWCNTs, which proves the competing of two conductance mechanisms. It should be noted that in the Sb₂Te₃-MWCNT, a weak antilocalization (WAL) effect with a magnitude of ~0.03% was observed at 2 K (Figure 4f, inset). Typically, the WAL effect of an order of magnitude higher value is observed for the Sb₂Te₃ flakes of thicknesses ~25 nm [43]. The appearance of the WAL in the magnetoresistance curves of Sb₂Te₃-MWCNT networks may be related to the tuning of the Fermi level of Sb₂Te₃ as a result of the charge transfer at

the Sb_2Te_3 interface, resulting in the ability to observe topological properties of the Sb_2Te_3 nanostructures [59].

In contrast to the Sb₂Te₃-MWCNT heterostructured networks, both p-type and n-type Bi₂Se₃-MWCNT heterostructured networks (Figure 4e,d) exhibited negative magnetoresistance in the entire temperature range from 2 K to 300 K at magnetic fields higher than ± 0.5 T, reaching ~-10% and ~-5%, respectively, at the maximal magnetic field of ± 9 T. Presumably, the negative magnetoresistance of the p-type Bi₂Se₃-MWCNT heterostructured network, which is similar to the magnetoresistance of the bare MWCNT network (Figure 4a,e), indicates the dominating role of MWCNTs in the conductance of this heterostructured network with a minor contribution from the Bi₂Se₃ nanostructured network. In turn, the negative magnetoresistance of n-type Bi₂Se₃-MWCNT (Figure 4f) is ~50% lower in comparison with the magnetoresistance of the p-type Bi₂Se₃-MWCNT heterostructured network (Figure 4e) and bare MWCNT network (Figure 4a). This may indicate the influence of MWCNTs' contribution of Bi₂Se₃ nanostructures in the total conductance of this sample, which is significantly more pronounced in comparison with the p-type Bi₂Se₃-MWCNT heterostructured networks and may arise from the interconnected few nm thin Bi₂Se₃ layers coating the surfaces of MWCNTs [16]. The contribution of the Bi₂Se₃ nanostructures to the total conductance of Bi₂Se₃-MWCNT heterostructured samples is also indicated by WAL cusps, which were observable for both p-type and n-type Bi₂Se₃-MWCNT heterostructured networks at low temperatures and magnetic fields lower than ± 0.5 T (Figure 4e,f, insets) and were typically observed for Bi₂Se₃ nanostructures and thin films. For the p-type Bi₂Se₃-MWCNT, the WAL cusps were less pronounced and observed at temperatures below 5 K (Figure 4e, inset). In turn, for the n-type Bi₂Se₃-MWCNT heterostructured networks, the WAL cusps had ~three times higher intensity (Figure 4f, inset) and were detectable at higher temperatures compared with the p-type Bi_2Se_3 -MWCNT (≤ 10 K vs. ≤ 5 K for n-type and p-type Bi₂Se₃-MWCNT networks, respectively). Data on the magnetoresistance of different samples at 2 K are summarized in Table 2.

Sample	MR, %	WAL	Comment	
MWCNT networks, this work	-10	no		
MWCNTs/polyvinyl acetate [53]	-3	no	Low magnetoresistance may be related to the impact of the binder	
Sb2Te3, this work	+10	no		
Sb2Te3, PVD grown [43]	+50 +100	yes/no	0.25% WAL observed only for the 25 nm thin flake.	
Bi2Se3, this work	+30	yes		
Bi2Se3, MBE grown [23]	+5	yes	For thicknesses < 100 nm	
Sb2Te3-MWCNT, this work	-1.1	yes	MR upturn at high (>6 T) magnetic fields	
p-type Bi2Se3-MWCNT, this work	-11	yes	WAL + 0.03%	
n-type Bi2Se3-MWCNT, this work	-5	yes	WAL + 0.2%	

Phase coherence lengths estimated from the Hikami–Larkin–Nagaoka (HLN) equation's fit (Figure 5a) for magnetoconductance [60]:

$$\Delta G(B) = -\alpha \frac{e^2}{\pi h} \left[\psi \left(\frac{1}{2} + \frac{\hbar}{4e l_{\phi}^2 B} \right) - ln \left(\frac{\hbar}{4e l_{\phi}^2 B} \right) \right]$$

where ψ is the digamma function, α is a prefactor depending on the contribution of competing conduction channels, and l_{ϕ} is the phase coherence length, which exhibited a power

law behavior for both p-type and n-type Bi₂Se₃-MWCNT networks with the relationships $l_{\phi} \sim T^{-0.46}$ and $l_{\phi} \sim T^{-0.59}$ (Figure 5b), which are close to the theoretical power law dependence of $l_{\phi} \sim T^{-1/2}$ for 2D topological insulator systems [27]. This indirectly proves that the WAL at low magnetic fields may originate from the 2D surface states of Bi₂Se₃ nanostructures.



Figure 5. (a) The change in magnetoconductance of the n-type Bi_2Se_3 -MWCNT heterostructured network, which fits the HLN theory for the temperatures 2–5 K; (b) the temperature dependence of the phase coherence length l_{ϕ} of p-type and n-type Bi_2Se_3 -MWCNT heterostructured networks.

The range of temperature-dependent l_{ϕ} was 60–150 nm for p-type Bi₂Se₃ MWCNT networks and 80–200 nm for n-type Bi₂Se₃-MWCNT networks, which is in line with the l_{ϕ} values reported for the Bi₂Se₃ nanostructures (l_{ϕ} ~100–200 nm) [61]. Higher l_{ϕ} values of the n-type Bi₂Se₃-MWCNT network in comparison to those of the p-type Bi₂Se₃-MWCNT network could be related to the higher amount of Bi₂Se₃ in the n-type network, resulting in an increase in the interconnections between the Bi₂Se₃ nanostructures and the formation of larger Bi₂Se₃ clusters.

The determined negative values of prefactor α varied from -0.02 to -0.1 for the p-type Bi₂Se₃-MWCNT network and around -0.02 for the n-type Bi₂Se₃-MWCNT network (Table 3), which is significantly smaller than the typical α values, ranging from -0.5 to -1.5 and suggesting single ($\alpha = -0.5$) or multiple ($\alpha = -1$; -1.5) independent bands with WAL [62].

Т, К	p-Type Bi ₂ Se ₃ -MWCNT Network		n-Type Bi ₂ Se ₃ -MWCNT Network	
	l _{\$\phi\$} , nm	α	l _{\$\phi\$} , nm	α
2	148	-0.02	197	-0.02
3	82	-0.1	192	-0.021
4	64	-0.1	125	-0.025
5	111	-0.02	118	-0.024
10	-		82	-0.023

Table 3. Phase coherence length l_{ϕ} and prefactor α determined using the Hikami–Larkin–Nagaoka theory for p-type and n-type Bi2Se3-MWCNT networks for the 2–10 K temperature range.

Presumably, close-to-zero values of prefactor α may indicate the contribution of both weak localization (WL), originating from MWCNTs [28–30], and WAL, originating from Bi₂Se₃ nanostructures. It was shown previously that the WL and WAL may coexist in the quantum diffusion regime in systems where the mean free path of the charge carrier due to elastic scattering is much shorter than the sample size, but the phase coherence length l_{ϕ} due to inelastic scattering is comparable with the sample size. The transition from WAL to WL corresponds to the change in prefactor α in the HLN formula from a negative to a

positive value [62]. In addition, the thickness-dependent transition of WAL to WL was also previously observed for Bi₂Se₃ films grown via PVD on graphene substrates and explained by the dependence of the band bending of Bi₂Se₃/graphene and Bi₂Se₃/air interfaces on the thickness of the Bi₂Se₃ film [63]. It should be noted that, as revealed in the Sb₂Te₃-MWCNT and Bi₂Se₃-MWCNT heterostructured networks, the contribution of 2D topological states of the Sb₂Te₃ and Bi₂Se₃ expressed by the appearance of WAL at low temperatures may open the path for the further enhancement of the thermoelectrical properties of such networks via the optimization of the geometry (in particular, the thickness) of the deposited nanostructures, as well as the TI:MWCNT mass ratio [7,64].

4. Conclusions

The resistance and magnetoresistance of thermoelectric p-type Sb₂Te₃-MWCNT (S~74 µV·K⁻¹), p-type Bi₂Se₃-MWCNT (S~11 µV·K⁻¹), and n-type Bi₂Se₃-MWCNT $(S \sim -52 \ \mu V \cdot K^{-1})$ heterostructured networks prepared via the direct physical vapor deposition of Sb₂Te₃ and Bi₂Se₃ nanostructures on MWCNT networks were measured in the 2 K to 300 K temperature range and compared with the properties of bare MWCNT networks (S~16 μ V·K⁻¹) and the reference Sb₂Te₃ and Bi₂Se₃ nanostructured thin films revealed the conductance governing mechanisms in these heterostructured networks and their contribution to the thermoelectric properties. It was found that in the Sb₂Te₃-MWCNT and Bi₂Se₃-MWCNT heterostructured networks, the conductance at different temperatures is governed by different mechanisms and different components of this network. In Sb₂Te₃-MWCNT networks, the conductance at temperatures ranging from 150 K to 300 K temperatures is dominated by the Sb₂Te₃ nanostructures, resulting in a high Seebeck coefficient of the Sb₂Te₃-MWCNT network and lower in comparison to the bare MWCNT network resistance, which may be favorable for the applications of Sb₂Te₃-MWCNT networks in flexible thermoelectrics. Below 150 K, the resistance curve showed a gradual upturn, indicating the decreasing contribution of Sb_2Te_3 to the conduction. At temperatures below 30 K, the conductance in these heterostructured networks is mainly governed by the MWCNT network except at the lowest measurement temperature of 2 K, where a low-intensity WAL cusp was observed, indicating the possible minor contribution of the surface states of Sb₂Te₃ to the conduction. In contrast, the conductance mechanisms in p-type and n-type Bi₂Se₃-MWCNT heterostructured networks were found to be more sophisticated. In these networks, the amount of the deposited Bi₂Se₃ material determined the magnitude of its contribution to the total conductance. It was found that in p-type Bi₂Se₃-MWCNT heterostructured networks, the dominant contributor to the conductance of the network in the entire temperature range from 2 K to 300 K were MWCNTs with a minor contribution from Bi_2Se_3 nanostructures, expressed in the lower by the ~30% Seebeck coefficient in comparison to the bare MWCNT networks and appearance of lowintensity WAL cusps in the magnetoresistance curves measured at temperatures below 5 K, indicating the contribution of the 2D surface states of Bi₂Se₃. By contrast, in the n-type Bi₂Se₃-MWCNT heterostructured network, which was prepared using a higher amount of Bi₂Se₃, the total conductance is the result of the competing contributions of the MWCNT network and Bi₂Se₃ nanostructured network, leading to the significant negative Seebeck coefficient accompanied by the increased resistance of the heterostructured network. The magnitude of WAL observed in the magnetoresistance curves of the n-type Bi₂Se₃-MWCNT heterostructured networks was significantly higher in comparison with the other heterostructures studied in this work and was observed at higher temperatures (below 10 K). Presumably, the difference between the p-type and n-type Bi₂Se₃-MWCNT heterostructured networks is in the type of contribution made by the Bi₂Se₃ nanostructures. In the p-type Bi₂Se₃-MWCNT networks, the Bi₂Se₃ contribution may arise from the network of interconnected free-standing Bi₂Se₃ nanostructures. In contrast, in the n-type Bi₂Se₃-MWCNT networks, this contribution may come from the interconnected few nm thin layers of Bi₂Se₃ surrounding the MWCNTs. In the latter case, separate n-type conductive channels may be formed at the MWCNT/Bi₂Se₃ interface, which leads to the n-type conductance of this network. The fitting of the low-temperature magnetoconductance of the p-type and n-type Bi₂Se₃-MWCNT heterostructured networks to the Hikami–Larkin–Nagaoka (HLN) theory confirmed the contribution of the 2D surface states, originating from the Bi₂Se₃ component of the heterostructured networks. In addition, the fit to the HLN indicated the possible co-existence of WAL and WL in these heterostructures, which may originate from Bi₂Se₃ nanostructures and MWCNTs, respectively. These findings open the path for further research and the optimization of TI-CNT heterostructures for application in flexible thermoelectrics and, as revealed in this work, the contribution of topological states to their conducting mechanisms may significantly improve the thermoelectrical properties of the heterostructured networks.

Author Contributions: Conceptualization, D.E.; methodology, J.A., K.B. and D.E.; investigation, K.B., J.A., E.S. and A.F.; Visualization, K.B. and E.S.; writing—original draft preparation K.B. and J.A. with the contributions from all authors; writing—review and editing, D.E.; supervision, D.E. All authors have read and agreed to the published version of the manuscript.

Funding: This work was funded by the European Regional Development Fund (ERDF) project No. 1.1.1.1/19/A/138.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Data are contained within the article.

Acknowledgments: The authors acknowledge Liga Jasulaneca for her assistance with the experiments and data analysis.

Conflicts of Interest: Authors Krisjanis Buks and Elmars Spalva were employed by the company 3D Strong Ltd. The remaining authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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Perovskite Topological Lasers: A Brand New Combination

Liangshen Wang, Lijie Wu and Yong Pan *

College of Science, Xi'an University of Architecture & Technology, Xi'an 710055, China; myoptics@xauat.edu.cn (L.W.); wulijieli@xauat.edu.cn (L.W.)

* Correspondence: panyong@xauat.edu.cn

Abstract: Nanolasers are the essential components of modern photonic chips due to their low power consumption, high energy efficiency and fast modulation. As nanotechnology has advanced, researchers have proposed a number of nanolasers operating at both wavelength and sub-wavelength scales for application as light sources in photonic chips. Despite the advances in chip technology, the quality of the optical cavity, the operating threshold and the mode of operation of the light source still limit its advanced development. Ensuring high-performance laser operation has become a challenge as device size has been significantly reduced. A potential solution to this problem is the emergence of a novel optical confinement mechanism using photonic topological insulator lasers. In addition, gain media materials with perovskite-like properties have shown great potential for lasers, a role that many other gain materials cannot fulfil. When combined with topological laser modes, perovskite materials offer new possibilities for the operation and emission mechanism of nanolasers. This study introduces the operating mechanism of topological lasers and the optical properties of perovskite materials. It then outlines the key features of their combination and discusses the principles, structures, applications and prospects of perovskite topological lasers, including the scientific hurdles they face. Finally, the future development of low-dimensional perovskite topological lasers is explored.

Keywords: photonic chip; nanolaser; topological laser; perovskite

1. Introduction

Recently, there has been an increasing worldwide curiosity in cutting-edge science and technology, encompassing advancements such as photonic chips and quantum computing. The swift advancement of photonic chip technology is vital in a range of fields, ranging from national defence science and technology to industrial engineering, medical, healthcare and communication transmission [1]. To tackle the current scientific challenges presented by photonic chips, it is essential to prioritise the research on their fundamental component: the low-dimensional laser light source [2]. Unlike traditional lasers, low-dimensional lasers are micro- and nanoscale in size. They can be divided into the following two main categories: In the first category, a specific material acts as both a gain medium and a resonant cavity. When the material is excited, it can be directly oscillated and amplified [3]. The second category involves two different materials acting as the gain medium and the resonant cavity and operates on the same emission principle as macroscopic lasers [4]. Recent advances in integrated photonic/quantum chips require low-dimensional light sources to achieve a threshold below kW/cm^2 [5,6]. Smaller sizes are preferred if the output quality is assured. Based on reference [6], reduced threshold and improved stability in a light source can result in reduced power consumption, faster signalling, faster chip operation and improved parallel computing capability and transmission efficiency. However, the advances in chip technology are still limited by various factors like the quality of the optical cavity in the light source and the operating threshold and mode. The absence of a novel excitation method that fulfils the laser operational requirements for low energy consumption whilst remarkably reducing the device's size is deemed a major hindrance, as reported in [7].

Citation: Wang, L.; Wu, L.; Pan, Y. Perovskite Topological Lasers: A Brand New Combination. *Nanomaterials* **2024**, *14*, 28. https:// doi.org/10.3390/nano14010028

Academic Editors: Jose Maria De Teresa, Marco Anni, Ricardo Lopez Anton and Sion Federico Olive Méndez

Received: 16 October 2023 Revised: 14 December 2023 Accepted: 18 December 2023 Published: 21 December 2023



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The development of topological optics has led to innovative ideas for new excitation mechanisms for low-dimensional lasers [8]. Topological lasers emit coherent light using their non-trivial energy band topology. This makes them robust to disorders and defects [9]. This topological protection significantly improves laser performance and allows for singlemode lasers with high robustness [10]. For example, topological photonic crystals can achieve efficient utilization of light energy by modifying the wave-particle duality of photons. This could solve the above-mentioned bottleneck [11]. Currently, research on topological nanophononics is not only addressing the issues of low-dimensional laser size and performance but also paving the way for large-scale integrated optical chip light sources [12]. In general, halide perovskites have the formula ABX_3 , where A is a monovalent cation, such as formamidine (FA⁺), methylammonium (MA⁺), caesium (Cs⁺) or rubidium (Rb⁺), and B is a divalent metal cation. Such as tin (Sn²⁺), bismuth (Bi^{3+}) or lead (Pb^{2+}) , and X is a halogen anion, such as chlorine (CI^{-}) , bromine (Br^{-}) , iodine (I⁻) or mixtures thereof. Depending on the composition, the usually perovskites can be divided into the following two categories: organic-inorganic hybrid perovskites and pure inorganic perovskites. These materials have attracted attention in the context of gain media due to their distinctive laser gain properties, including high quantum yield, wide bandgap tunability and easy absorption properties [13]. Since 2019, various types of perovskite materials have demonstrated significant potential as laser-active region dielectric materials. Compared to many other active materials, the solution-treated films of these materials have the advantages of large optical absorption cross-section, large exciton binding energy, high photoluminescence quantum yield, high defect tolerance, and device tunability, making their role as a laser gain medium unparalleled [14]. As a result, the combination of topological optics and perovskite is set to lead to new breakthroughs in the research of micro- and nanolasers [15]. Thus, summarizing the topological lasers of low-dimensional perovskites is crucial.

This study focuses on low-dimensional lasers using perovskite material as the primary gain medium and the topological mode as the excitation. Recent advances in perovskite topological lasers are summarised in terms of their principle, structure, application and prospects. This paper aims to introduce the coupling principle of perovskite materials and topological laser modes. It does so by summarising the current research on perovskite topological lasers and, accordingly, by expanding the depth of research at the photonic quantum scale. The study provides some ideas for the advancement of research on perovskite topological lasers. Figure 1 shows the milestones in the development of topological lasers in recent years [7–12].



Figure 1. Recent process summarizes in topological lasers. Schematic of the CsPbBr₃ Perovskite Quantum Dot Vertical Cavity Lasers, reproduced with permission from [7], copyright 2017, *ACS Photonics*. Laser mode in a topological cavity, reproduced with permission from [8], copyright 2018,

Science. Schematic of the photonic crystal-based topological insulator, reproduced with permission from [9], copyright 2019, *Nature Nanotechnology*. Topological laser in a directional outcoupling configuration, reproduced with permission from [10], copyright 2020 *Nature*. Topological-cavity surface-emitting laser structure with the vertical-mode profile in green, reproduced with permission from [11], copyright 2022, *Nature photonics*. Illustration of the 2D perovskite lattice embedded between distributed Bragg reflectors (DBRs), reproduced with permission from [12], copyright 2023, *Science Advances*.

2. Fundamental Principles of Topological Lasers

A laser is a coherent light source with exceptional luminous intensity and perfect directionality. A basic laser system comprises a pump source, gain medium and resonator. This three-part system is widely recognized within the field. In this systematic arrangement, the pump source provides the light source for the laser, while the gain medium absorbs the energy provided by the pump source and enhances the light. The resonator functions as the circuit between the pump source and the gain medium, and the output laser is chosen by oscillating the cavity [16]. Topology pertains to the examination of the characteristics of geometric figures or spaces that can retain their structure after being subjected to continuous shape changes. It focuses solely on the spatial relationships between objects, regardless of their shape and size [17]. As the notion of topology broadened from condensed matter physics to photon physics, a new genre of laser, known as the topological laser, emerged. The laser was inspired by the discovery of a topological insulator, in which interface electrons do not dissipate even in the presence of impurities. Similarly, a well-designed wave vector space topology can be used to create optical transport interfaces that support useful and interesting properties. In particular, this suggests that unidirectional waveguides allow light to flow around large defects without back reflection. Other types of topological lasers are also used for display purposes, the light can efficiently be directed around corners and defects, moving in a constant direction at the optical waveguide's edge [18].

To date, the comparison system categorises topological lasers into the following three distinct categories: topological insulator lasers, topological defect lasers and radiation topological lasers. The first category can be further subdivided into quantum Hall lasers, quantum spin Hall lasers, quantum valley Hall lasers and lasers based on Su-Schrieffer-Heeger (SSH)-like models. The topological insulator laser uses a topologyprotected edge mode laser to effectively bypass defects and corners. Among them, the topological edge state appears in the spatial boundary between the systems with different topologies, and the energy of the edge state is located in the gap of the bulk bands [19,20]. The continuous system of a laser with topological defects is quenched to an ordered state by competing time scales during the phase transition. These defects limit the consistency of the system and its ability to approach a fully ordered state, the free spectral range is larger than the conventional micro-/nanowire cavity, so it is more likely to support singlemode laser emissions in a specific spectral gain window [21]. The radial and azimuthal polarization vector beams can be directly emitted by the radiation topological laser with square lattice photonic crystals to manipulate the polarization and angular momentum of the light with non-trivial topological charges [22,23]. Quantum Hall lasers combine two photonic crystals with different topologies, one with a non-trivial topology activated by an external magnetic field and the other with trivial topology, the photon Quantum Hall effect dictates that a topologically protected edge mode must exist along the interface [19,24]. Photons in a photonic system can exhibit spin-like quantities, called pseudo-spins, which are represented by two internal states (e.g., two polarised states or two orbital modes in a cavity). Spin-momentum locked edge mode lasers are typical of quantum spin Hall lasers. These devices consist of two cellular lattice photonic crystals (PhC), in which the inner and outer PhC regions have the same bandgap, but the topology is different [25]. The room temperature laser from the photonic Valley Hall nanocavity, based on the quantum Valley Hall effect, has a narrow spectrum, high coherence and threshold behaviour. The emitted beam has a singularity encoded by the three-terminal cavity mode, which exists in the bandgap

of the two Houle periodic photonic lattices with opposite parity disorder [26]. The orbital version of the SSHHamiltonian is realised in a one-dimensional polaron microcolumnar lattice, where laser emissions from the topological edge state persist despite local lattice deformation. Under non-resonant optical pumping, the gain occurs in the topological edge state. The topological robustness of the laser interaction to the optically induced lattice deformation is then demonstrated using the polariton interaction [27]. Irrespective of the laser's topology, the resonator's structure has been enhanced to attain more efficient and stable optical resonance and beam quality. Selecting the appropriate gain medium is vital to the laser's performance and output characteristics.

Generally, gain media must fulfil basic requirements such as high triplet level, low excitation threshold, good spectral matching and effective population inversion [11]. Perovskites can be classified into the following four types based on their dimensionality: 0-dimensional quantum dots, 1-dimensional structures, 2-dimensional microstructures and 3-dimensional structures. The quantum dots that won this year's Nobel Prize in Chemistry are small but powerful semiconductor particles with exceptional optical and electronic properties, typically less than 20 nanometres in size. To put this in perspective, they are 110,000 times smaller than the diameter of an average human hair. Because of their tiny size, quantum mechanics comes into play when measuring their properties. The 0D perovskite quantum dots (QDs) have found wide application in lasers due to their remarkable properties, including convenient synthesis, high luminescence quantum yield, robust tolerance to defects and tunable bandgap of different elements [28]. One-dimensional (1D) perovskite, when used as the gain medium in a topology laser, boasts various advantageous characteristics, including the ability for a micro-laser with an ultra-thin gain medium (<50 nm) to produce single-mode emission with a low laser threshold (6.8 μ J/cm²). In addition, laser emission can be continuously tuned in the gain spectrum range (from λ = 532 to 519 nm) by altering the thickness of the gain medium. This innovation addresses common issues found in thick quantum dot films, such as poor uniformity, aggregation and luminescence quenching [29]. In the two-dimensional structure of perovskite, the nanostructures—known as nanoplates (NPL)—sustain quantum confinement in a singular direction. The electronic properties of these materials are characterised by narrow emission lines at low and room temperatures, with significantly improved exciton binding energy and absorption cross sections (corresponding to the area of NPL) compared to colloidal quantum dots. Additionally, the low threshold for amplified emission and optical gain coefficient provided by simultaneous one-photon and two-photon absorption pumping is approximately four times greater than that offered by the colloidal quantum dots [30]. Although 3D perovskite possesses a high optical gain and a low threshold, it can only achieve high-efficiency laser emission due to its narrow band gap and poor thermal conductivity. This hinders its ability to achieve high-energy laser emission and adversely affects its performance and operational life [31]. After careful consideration and thorough comparison, our recommendation is to utilize a sub-2D low-dimensional perovskite as the gain medium.

The reason why the combination of low-dimensional perovskites and topological lasers can be improved is mainly due to the special properties of low-dimensional perovskites and the unique properties of topological lasers. First, low-dimensional perovskites have smaller dimensions, usually only a few nanometres to a few hundred nanometres, and therefore have a higher specific surface area and quantum confinement effects. These properties make low-dimensional perovskites have a higher optical gain and a lower threshold, and can realise high-efficiency laser emissions [32]. Secondly, the topological laser uses the edge states in the topological material to realize the unidirectional transmission of light. It has a strong robustness and can keep stable performance under the design of different geometric resonators [33]. The combination of low-dimensional perovskite and topological laser can make full use of the advantages of both to achieve high efficiency, high power, low threshold, stable and tunable laser emission, expanding the application of topological laser.

Table 1 summarizes the performance comparison of nanolasers with different working materials reported in recent years. Nanolasers are similar to the gain medium used in

Ga_{0.05}Al_{0.95}As/Ga_{0.8}Al_{0.2}As

CsPbBr₃

200 µW

8.95 μJ/cm²

zero topology lasers and have some reference value. It is not difficult to see from Table 1 that nanolasers with perovskite gain medium do not have a high-quality factor, but they do have a visible emission wavelength, which is of great importance for future applications. The topology of the laser is very conducive to the optical emission of the perovskite (structure) material. On the one hand, perovskite (structure) quantum dots can effectively absorb light energy and generate excitons due to their excellent optical and chemical properties, large light absorption cross-sections and exciton binding energy. On the other hand, the wavelength of the quantum dots can be tuned to the blue spectral region, resulting in a broad spectrum of light emission. Topological lasers rely on structural robustness to achieve high-efficiency beam delivery. As an example, topological photonic crystals are composed of a series of hexagonal rings. Each ring is coated with a layer of material doped with fluorescent substances, forming a miniature resonant cavity [34]. When light hits the topological photonic crystal, the vibrational modes and interaction laws of the fluorescent substance differ from those of ordinary light. This leads to a reduction in the probability of reflecting, scattering or absorbing a photon, resulting in q highly efficient beam transmission [35]. For clarity, consider a magneto-optical crystal consisting of a square lattice of yttrium–iron–garnet (YIG) rods with a radius of 0.11 α in air, where α is the lattice constant. An external direct-current magnetic field applied in the out-of-plane (z) direction induces strong gyromagnetic anisotropy, with the permeability tensor taking the form (1):

$$u = \begin{bmatrix} u & ik & 0 \\ -ik & u & 0 \\ 0 & 0 & u_0 \end{bmatrix}$$
(1)

In the above formula, *k* and *u* represent the permeability tensor, *i* is the imaginary unit, and u_0 is the permeability in vacuum. With a 1600 Gauss applied field, the tensor elements in YIG at 4.28 GHz are $k = 12.4u_0$ and $u = 14u_0$. This formula ignores the effects of material dispersion and loss and assumes that there are frequency-independent permeability tensors with real *k* and *u* values. Due to the existence of magnetic anisotropy, we have to apply the following traditional band theory of photonic crystals to the system: we remove the magnetic field from the Maxwell's equations to obtain the following master Equation (2):

$$\nabla \times (u^{-1}(r)\nabla \times E) = \varepsilon(r)\omega^2 E \tag{2}$$

2021

2023

[27]

[17]

Here, the inverse permeability tensor $u^{-1}(r)$ and the scalar permittivity $\varepsilon(r)$ are both functions of position, and ω is the mode frequency, and *E* is electric-field strength [36,37].

Published Output Gain Medium Threshold **Q**-Factors Refs. Wavelength (nm) Year Oregon Green 488 0.005 mJ 14.8 531 2009 [38] 510 InGaN@GaN 3.7 kW/cm² ~17 2012 [39] CH₃NH₃PbBr₃ 59 uJ/cm² ~855 ~552 2016 [40] PMMA:DCM 5.6 MW/cm² 2017 310 ~643 [41]NaYF4:Yb3+/Er3+ 70 W/cm² >200 664 2019 [42] InAsP/InP ~12.5 kW/cm² ~35,000 ~1550 2019 [43]

~72,000

~5000

Table 1. Comparison of different gain media in a nanolasers.

The transverse magnetic mode in a rotating magnetic photonic crystal can be formally mapped to the electron wave function in a periodic electromagnetic field, so the only requirement for the existence of a unidirectional edge mode is that the Chern number in all frequency bands below the gap is non-zero. In a two-dimensional system, the first Chern number characterizes the topological invariant, which is proportional to the Berry phase

754

515

that encloses the first Brillouin zone. We can express the integral form of the topological Chern number in Equation (3).

$$C_n = \frac{1}{2\pi} \int\limits_{BZ} d^2 k \Omega_n(k_x, k_y) \tag{3}$$

Here, C_n is the Chern number, π is the Pi, $\Omega_n(k_x, k_y)$ is the Berry curvature, k_x and k_y are the crystal momentum k varying in the x and y directions, respectively, in the first Brillouin zone. According to the description of an integral quantum Hall state in band theory, it occurs when an electron confined to two dimensions is placed in a strong magnetic field. The quantization of an electron's circular orbit with a cyclotron frequency ω_c leads to a quantized Landau energy level of $\varepsilon_m = \hbar \omega_c (m + 1/2)$. If *N* Landau levels are filled and the remaining levels are empty, the gap will be separated from the occupied state as in an insulator. Unlike insulators, however, electric fields can cause cyclotron orbital drift, producing Hall currents characterized by quantifying Hall conductivity. Therein, Hall conductance is a physical quantity that measures the rate of change in current produced by the Hall electrode. It is an important parameter of the Hall effect and can be used to measure magnetic field, conductivity and other physical quantities. Its expression can be found in Equation (4) [44,45].

$$\sigma_{xy} = -\frac{e^2}{h} \sum_n C_n \tag{4}$$

Here, σ_{xy} is the hall conductance of two-dimensional insulators, *e* is basic charge, *h* is the Planck's constant. The quantization of σ_{xy} has been measured to 1 part in 10⁹. This precision is a manifestation of the topological nature of σ_{xy} [46].

Topological lasers are lasers that function using topologically protected edge-state currents. These edge-state currents travel in semicircular trajectories along the edges of topological insulators and are not susceptible to interruptions from impurities or defects [47]. Photons do not have magnetic moments and are, therefore, not directly affected by magnetic fields. However, a similar effect can be achieved by electrons excited by incident light. The magnetic field affects these electrons differently, so the light is also affected differently [48]. The principle of topological lasers is closely related to their pumping method, as mentioned in reference [14]. To pump a topological laser, energy must be injected into the topological insulator to excite the electrons and initiate the topologically protected edge state currents. The pumping method can be either electrical or optical. In electrical pumping, the electrons in the gain medium material are excited by incident light, which creates a jump and is then stimulated to emit radiation (as stated in reference [49]). The topological cavity surface-emitting laser (TCSEL) is a low-dimensional device that generates nanolasers by optical pumping, combining the structure of vertical surface-emitting lasers with the topological laser mode, as stated in reference [50]. To generate a stable single-mode laser over a larger area of the chip, the authors and their team successfully tackled this challenge by implementing a Paul Dirac vortex topology cavity. To be specific, to achieve far-field size emission above 500 µm with narrow scattering angles and to lower the excitation threshold for optical pumping (Figure 2a) [11], the effective size of the device is continuously increased by adding more photonic crystal cycles to its structure. In contrast to electric pumping that injects electrons and holes to make the gain medium absorb energy, the electrons of the gain medium of an electrically pumped terahertz are excited by applying voltage across the topological insulator [51]. Zeng et al. at Nanyang Technological University, Singapore, and Chattopadhyay et al. at the University of Leeds, United Kingdom, reported a terahertz laser based on the boundary states of the topological valley in 2020, as shown in Figure 2b [10]. An investigation into a two-dimensional bandgap valley material led to the creation of a compact photonic crystal with valley degrees of freedom. By simply superimposing one side of the device, it can be seen that each laser mode emits almost the same intensity from both sides. Consequently, the left- and right-handed cavity modes are both of equal intensity and are protected by the topology. To achieve effective energy

transfer and topology-protected initiation of edge-state currents, it is, therefore, essential to select the appropriate light source and material for each of the two pumping modes [52].



Figure 2. (a) Pattern analysis of TCSEL, reproduced with permission from [11], copyright 2022, *Nature photonics*. (b) A THz quantum cascade laser with topologically protected valley edge states, reproduced with permission from [10], copyright 2020, *Nature*.

Aside from conventional pump sources, chemical and nuclear excitation methods also exist. To enhance the coherent light produced by the pump source, a gain medium, as stated in reference [53], is indispensable. At present, silica and perovskite are the two main types of laser gain media that exhibit superior performance in producing topological laser modes. Figure 3a shows a topological cavity that carries a photonic MZM [54]. Three-well resonant phonon GaAs/Al_{0.15}Ga_{0.85} terahertz QCL chip, such as the one used in this work, which is created by the passage of light through the top metal layer and hexagonal air-hole lattice of a terahertz QCL wafer. This structure effectively reduces intracavity reflection and loss, thereby improving the laser's performance in terms of output and excitation. Due to the high refractive index property of silica, the laser output power and energy can be improved to some extent. However, the excessive refractive index of silica causes the light to be confined, resulting in insufficient oscillation capability, making it difficult to achieve low-threshold operation for topological lasers with silica as the gain medium in new photonic chips that require low energy consumption; therefore, a new material substitution is urgently needed [55].



Figure 3. (a) Electro-pump quantum cascade laser (QCL) based on photonic Majorana zero-mode (MZM), reproduced with permission from [54], copyright 2023, *Nature Communications*. (b) Schematic representation of perovskite metasurfaces supporting spin-valley locking emission, reproduced with permission from [56], copyright 2023, *Nature Materials*.

In a topological laser, external excitation sources (such as light) excite the atoms or molecules in the perovskite material to high energy states. An ultrathin gain medium of all-inorganic caesium-lead-halide perovskite quantum dots is used to reverse the number of particle distributions, enabling laser amplification and emission [57]. The optical pumping mechanism of perovskite is influenced by its energy level structure, external factors such as temperature and pressure, and particle interactions. In addition, the topology of the perovskite can also influence the optical pumping mechanism. For example, a non-banal topology can improve the optical localisation and efficiency of optical pumping, ultimately leading to improved laser performance. The interface between perovskite and other materials affects the optical pumping mechanism, including charge and energy transfer. In addition, the spin-valley-locked perovskite mode has a topological structure that enables efficient and low-threshold broadband laser emission with tunable properties. Valley polarisation inversion is achieved by tuning the spin state, resulting in tunable nanolaser output. According to Figure 3b [56], the emission mechanism of spin valley-locked perovskite lasers is shown. The authors of the paper developed a self-limiting assembly method that allows for polycrystalline inclusion crystals to grow conformally within the hypersurface template. The conformal growth of the phenylethylammonium bromide (PEABr) inclusion ensures the conformal growth of inclusion crystals while limiting the grain size during the crystallization process. The characteristic size of the photonic structure can be as small as 50 nm, resulting in bright and uniform luminescence over a $40 \times 40 \ \mu\text{m}^2$ area. This study demonstrates compact spin-valley-locked perovskite emissive surfaces that assign spin-dependent geometrical phases to bound states in the continuum via Brillouin zone folding and process photons with different spins selectively to opposite valleys. This topology of spin-valley-locked perovskites is believed to create possibilities for tunable laser emission. This approach can generate entangled photon pairs on-chip for use as a light source for topological lasers and is also expected to contribute to the realization of chiral light-emitting diodes [58].

A well-designed resonant cavity, in addition to the effect of the gain medium, is critical in increasing the gain factor of low-dimensional topological lasers. When designing resonant cavities, the parameters of the mode type, length, width and mode are some of the factors to be considered. Spiral resonant cavities, electric dipole moment resonant cavities, lattice resonant cavities and others are some examples of resonant cavities. The helical resonant cavity is a type of structure that uses optical field interaction to produce optical phenomena. This structure has a high tuning sensitivity and stability, making it ideal for topological laser modes. Lin et al. [59], from the National Sun Yat-sen University in Taiwan, conducted a study wherein they designed an optical resonator that uses a helical phase defect to generate vortex lasers, as illustrated in Figure 4a. Figure 4b shows that the spiral-phase-defect (SPD) has topological charges of -1 and +1. The sign and size of the topological charge can be chosen for the resonant vortex mode. In addition, the authors used theoretical calculations to obtain a parameter space for generating vortex beams with variable topological charges. They have also demonstrated that the optical resonator can produce stable vortex beams in a 1064 nm vortex laser system, as depicted in Figure 4c.

A scalable order strategy was reported by Liao et al. [60] from Tsinghua University to achieve a stable on-chip integrated visible micro-nano laser. The improvement of laser performance was realised through enhancing the structural order (n) of specialized surfaces, generating desirable topological patterns. Figure 5a displays a schematic outline of the on-chip integrated laser mechanism, in which a femtosecond pump light with a wavelength of 400 nm enters the ring for excitation. Figure 5b presents the SEM top-view image of the CsPbBr3 microcavity coupling system in the integrated laser mechanism. The electric field distribution in the intrinsic mode of the on-chip integrated laser system is shown in Figure 5c, illustrating a microcavity radius of $1.5 \ \mu m$. The red arrow displays the time-averaged flow of power for the optical field in the microcavity, indicating strong unidirectional mode propagation. The lower right panel shows an enlarged view of the microcavity-MW coupling region. The above figure shows the simulated results of

the modal dispersion of the optical field in the cross section of the CsPbBr₃ waveguide (width: 150 nm; height: 300 nm), which are shown in the upper right section. The use of these resistors can lead to a significant improvement in the optical field quality factor and uniformity, which, according to the physical analysis, favours high-power and highbrightness laser applications. To achieve a higher optical field quality factor, it is necessary to optimise the resonator's physical structure and material selection. In addition, the optical field uniformity can be improved by precisely controlling the resonator's vibration modes. This study extends the research directions for non-Hermitian photonics in terms of nonlinear optics and topological photonics [61].



Figure 4. (a) Schematic representation of the laser formed by the pump mirror (PM) and the reflection type spatial light modulator (SLM). (b) Phase modulation provided by SLM and combining with limited helical and concave phases. (c) Phase modulation is provided by SLM and combines limited helical and concave phases, reproduced with permission from [59] copyright 2022, *IEEE Photonics Journal*.



Figure 5. On-chip integrated visible light micro-nano laser, reproduced with permission from [60], copyright 2023, *Science Advances*: (a) Schematic of excitation of 400 nm optical pumped laser. (b) Top view and 52° tilt scanning electron microscope (SEM) images of CsPbBr₃ microcavity coupling system (inset). (c) The electric field distribution of the intrinsic mode of a topological laser system is obtained by simulating the intrinsic frequency (the radius of the microcavity is 1.5 µm).

3. The Structure of Topological Lasers

In 2017, Bahari et al. [24] at the University of California, San Diego, CA, USA, demonstrated topological cavity lasers by combining geometrically independent and integrated nonreciprocal topological cavities (Figure 6a) with stimulated emissions from a unidirectional photonic edge state. The structures are made of InGaAsP multiple quantum wells (MQW), bonded on YIG grown on Gadolinium Gallium Garnett (GGG) by molecular beam epitaxy. An isolation ratio of over 10 dB was achieved at the output of a chosen waveguide. This experiment allows for the creation of intricate topological circuits with an arbitrary shape, which could greatly aid in the reliable and integrated transportation of photons in both classical and quantum regimes. In the subsequent year, the concept of topological insulator lasers was introduced by Harari et al. [8] (Figure 6b). Several types of topological lasers have been reported. This laser consists of several resonant rings. By adjusting the length of the resonant rings, an equivalent magnetic field is created that has opposite effects on clockwise and counterclockwise rotating light. Unlike the previous method, this laser breaks the symmetry of the time inversion of the photonic crystal [62], amplifying the pump light and eliminating the need for an additional static magnetic field, resulting in a double benefit. Moreover, by adding gains and losses to the structure, topologically protected lasing can be achieved without affecting the resulting topological properties, which is a theoretical breakthrough.



Figure 6. Schematic structure diagram of the topological laser: (**a**) A topological cavity of an arbitrary shape and an integration, reproduced with permission from [24], copyright 2017, *Science.* (**b**) Geometry and laser patterns of topological insulator lasers based on the Haldane model, (**A**) Cavity geometry (same for topological and trivial), (**B**) The steady state topological lasing mode of the topological cavity, reproduced with permission from [8], copyright 2018, *Science.*

Figure 7 displays the construction of a topological laser across various platforms. In their study, the authors designed a topological nanospace involving two types of PhC plates with square pores having the same period, but different unit cells, as depicted in Figure 7a [63]. While sharing a common band structure, the red and blue regions exhibit contrasting topologies, which are distinguished by the value of the two-dimensional Zak phase (θ_{Zak}), determined from the integration of the Berry connection within the first Brillouin zone. By suitably tuning the gap distance between the trivial and nontrivial parts of the PhC slab, a higher Q factor can be achieved. In addition, Figure 7b depicts the electric field distribution of the corresponding angular state, showing significant confinement in the nanoscale and resulting in strong light-matter interactions. This characteristic
has promising applications like developing topological nanolasers. Figure 7c illustrates a one-dimensional SSH structure [42]. The structure consists of linear chains of dimer unit cells comprising of identical resonators (with resonance frequency ω_0) having staggered nearest-neighbour coupling strengths. The capacitances used are $C_1 = C_3 = ---- = C_{odd} = C_A$ and $C_2 = C_4 = ---- = C_{even} = C_B$ (with C_A being greater than C_B). Figure 7d displays a one-dimensional non-Hermitian photonic lattice. It consists of 17 InGaAsP microrings (shown in red). Each microring consists of three microrings, exhibiting optical loss and gain, respectively [64]. The gain cavity comprises of an InGaAsP quantum well on an InP substrate, whereas the loss is realized by a layer of metal (Cr + Au) at the corresponding position.



Figure 7. Structural diagram of the topological laser (The scale bar is 1µm): (**a**) SEM image of a square two-dimensional topological PhC cavity. (**b**) Topological angular electric field distribution, reproduced with permission from [63]. Copyright 2020, *Light:Science & Applications*. (**c**) One-dimensional SSH structure consisting of linear chains of dimeric unit cells, reproduced with permission from [42], copyright 2019, *Light:Science & Applications*. (**d**) A one-dimensional non-Hermitian photonic lattice composed of 17 InGaAsP microloops, reproduced with permission from [64], copyright 2023, *Physical Review Letters*.

In 2017, a group led by Wang [65] at Nanyang Technological University in Singapore successfully developed vertical-cavity surface-emitting lasers (VCSELs) utilizing CsPbX₃ lead halide perovskite nanocrystals (IPNCs). These lasers are characterised by a low excitation threshold of 9 μ J/cm², a directional output with a beam dispersion of approximately 3.6 degrees, and exhibit good stability. In the same year, Huang's group [7] at the University of Washington in the United States reported an ultra-low lasing threshold of 0.39 μ J/cm². The research team created a VCSELs laser incorporating CSB-bBr₃ QDs in a thin film and two high-reflection distributed Bragg reflectors (DBRs). In 2023, Tian et al. from Nanyang Technological University in Singapore demonstrated a low-threshold single-mode laser emission with vertical emission. Their lithography-free, solution-processed and fully inorganic monolayer of lead halide perovskite quantum dots acted as an ultrathin gain medium. This experiment demonstrated the resilience of topological lasers to localised perturbations in multilayer structures. The cavity, as illustrated in Figure 8a, comprises an interface between two semi-infinite, one-dimensional binary photonic crystals, referred

to as PC1 and PC2, where PC2 has inversion symmetry along the z-direction. The LI and HI present near the inversion centre display different Zak phases in the lowest optical band because of their varied positions (Figure 8b). The one-dimensional topological cavity consists of two 10-unit half-cavities positioned at the centre of the first optical bandgap. At approximately 515 nanometres, it exhibits a high-quality interface state with a Q-value above 5000. The transmission spectrum calculated is illustrated in Figure 8c, with the electric field heavily confined to the interface of the two photonic crystals (PCs). Moreover, the asymmetrical distribution reaches its peak within the first Hole-Injection (HI) layer of PC1, which is depicted in Figure 8d.



Figure 8. Design principle of a 1D topological microcavity, reproduced with permission from 17, copyright 2023, *Nature Communications*: (a) A 1D topological microcavity formed by two photonic crystals (PC1 and PC2) composed of high refractive index (HI) and low refractive index (LI) layers. (b) Normalized electric field distribution of the first two optical bands along the *z*-axis within the respective cell. (c)The high Q interface state appearing within the optical band gap; (d) Spatial distribution of the electric field in the microcavity.

4. Applications and Prospects of Topological Lasers

Topological lasers are a novel optical device that offer several advantages, including high efficiency, power and beam quality [66]. As a result, topological lasers have found widespread application in all-optical switching, optical communication, TCSEL, Terahertz silicon interconnection technology, silicon-based photonic circuits and other areas.

Topological lasers accomplish the amplification and phase modulation of coherent light by generating phase and amplitude disparities on the surface of the laser cavity, enabling all-optical switching. The resulting phase-modulated light can be harnessed in all-optical switches, facilitating the processing and transmission of optical signals. Zhang et al. [67] reported the demonstration of linearly coupled antiregular polariton states, with ordered phase transitions and vortex-pair-petal states at the coalescence threshold, using a nonresonant ring pumping method in a planar perovskite microcavity (Figure 9a). In contrast with the uniform pumping in perovskite microcavities, which creates excitons throughout the microporous plates, toroidal pumping promotes the localised production of polarisable excitons (EPs). These EPs undergo repulsive interactions, leading to the toroidal localised blueshift and potential trap.



Figure 9. Application scenario of the topological laser: (a) A schematic representation of the formation of a petal-shaped condensed pattern, reproduced with permission from [67], copyright 2023, *ACS Photonic*. (b) Normalized electric field distribution of the first two optical bands along the *z*-axis within the respective cell, reproduced with permission from [68], copyright 2009, *Nature*. (c) Integrated of resonant second-order nonlinear optical devices, reproduced with permission from [69], copyright 2022, *Nature Communications*.

Optical communication: optical communication involves the transmission of optical signals from a transmitter to a receiver. Topological lasers are critical to optical communications because they produce highly efficient, high-power beams. The use of topological lasers enables longer transmission distances and higher transmission rates in optical communications. Wang et al [68] observed electromagnetic chiral edge states (CESs) for the first time by using magneto-optical (PhCs) fabricated in the microwave state. Similar to their electronic counterparts, these photonic CESs can only propagate in one direction. The team measured a difference of nearly 50 dB between forward and reverse transmissions, as seen in Figure 9b.

As a new generation of high-brightness surface emitters, TCSEL can be directly extended to any other wavelength range and has a very wide application prospect. It is capable of reaching 10 W peak power in a single device at 1550 nm, the wavelength at which fibre losses are minimal in global communications and the eye-safe wavelength for lidar in self-driving cars. It uses topological cavity technology, has a far-field divergence angle of less than 1° and a side-mode suppression ratio of 60 dB. It can integrate two-dimensional multi-wavelength arrays. The topological properties of TCSEL may mean that larger, more stable single-mode devices can be manufactured with better yield. In addition, it can integrate two-dimensional multi-wavelength arrays, and the topological properties of TCSEL can mean that larger, more stable single-mode devices have better manufacturing yields [11].

Silicon-based photonic circuits are a technology that utilizes silicon-based materials for photonic integration. They are programmable and scalable, making them an ideal platform for realizing photonic circuits. Figure 9c showcases an integrated, tens-of-microwatts, thin-film lithium niobate photonic circuit [69]. The circuit uses two input paths to drive

resonant cavities. These cavities exhibit fundamental and second harmonic frequencies, shown in red and blue, respectively. The researchers used tunable lasers operating at communication wavelengths to study second harmonic generation and cascade parametric oscillation processes through their optical paths. One of the input paths is connected to a shorter wavelength laser and is used to drive a direct optical parametric oscillator (OPO). Light is coupled in and out of the chip using a lensed fibre. The output light is separated and sent to silicon and InGaAs avalanche photodiodes [19], a free-space setup is used that has a dichroic reflector.

Terahertz Silicon Interconnection technology is a new communication technology that can realise high-speed, low-power, high-density data transmission in the terahertz frequency band. To meet the growing demand for high-speed, high-capacity consumer electronics products, increased interconnect capacity in terms of bandwidth density and active tunability is required to improve throughput and power efficiency. Low-loss, higher bandwidth terahertz silicon interconnects provide a solution to existing inter-chip/in-chip bandwidth density and power efficiency bottlenecks. Kumar et al. [69] proposed a low-loss terahertz topology interconnection-cavity system that can actively route signals via sharp turns via critical coupling to a topology cavity with an ultra-high quality (Q) factor of 0.2×10^6 . The topology cavity consists of a VPC waveguide closed loop (see Figure 10) with a Q of 0.2×10^6 , which is the first experimental proof of achieving ultra-high Q resonance at terahertz frequencies. In Figure 10a, the black and grey highlighted regions indicate the topologically distinct VPC domains formed by Type A and Type B unit cells, respectively. It is not difficult to see from Figure 10b,c that the peak frequencies of the two types of transmission intensities under low-power laser excitation are in good agreement.



Figure 10. All-optical control of a THz topological cavity-waveguide chip, reproduced with permission from [70], copyright 2022, *Advanced Materials*: (a) Artistic illustration of a valley photonic crystal (VPC) cavity-waveguide chip on an all-silicon (Si) platform. A continuous laser with wavelength 532 nm (energy 2.33 eV) photoexcites the Si above the bandgap (1.1 eV). The inset shows the unit cell of the VPC, where a denotes the periodicity and h represents the height equal to 200 µm. The unit cell contains two triangular air holes of side lengths I_1 and I_2 . $\delta = I_2 - I_1$ denotes the degree of asymmetry, with $\delta > 0$ and $\delta < 0$ corresponding to Type A and Type B VPCs (shaded in black and grey in the schematic). (b) Schematic illustration of THz intensity modulation caused by photoexciting the domain wall of VPC cavity (The black, red and blue lines represent the transmission intensity when $\delta > 0$, $\delta < 0$ and $\delta = 0$, respectively). (c) Schematic representation of frequency agility of the topological cavity resonance upon high-power photoexcitation.

5. Conclusions

This study presents an overview of the research progress made on topological lasers that utilize low-dimensional perovskite materials as the gain medium, and their main applications. Various models of topological lasers have been proposed, with varying materials and structural designs, from a theoretical perspective. Several types of topological lasers exist, such as photonic crystal-based, photonic insulator-based and topological phase-change lasers that incorporate photonic insulators and superconductors. Several research groups have successfully created topological lasers in their experiments, including those based on photonic crystals, photonic insulators with superconductors and phase-change lasers.

In conclusion, the combination of topological laser modes and perovskite materials displays efficient optical emission properties and excellent potential for photonic applications. The structure of topological lasers greatly promotes optical emission from perovskite materials. The perovskite quantum dots exhibit remarkable optical properties and chemical versatility, including a large optical absorption cross-section and exciton binding energy that allows for the efficient absorption of light energy and the generation of excitons.

In the future, research on the theory and experimental techniques to improve the performance and stability of these dots will focus on combining topological laser modes with Perovskite materials. Therefore, it remains imperative to further investigate the optical properties of low-dimensional perovskite materials and device preparation technologies for enhanced support and the facilitation of topological lasers' application in diverse fields. Topological lasers serve as an optimal on-chip light source option due to their low threshold, high efficiency, good directionality, high stability, compact size and cost-effectiveness.

Author Contributions: L.W. (Liangshen Wang): Study design, data collection, data analysis, data interpretation, formal analysis, data collection, data analysis, formal analysis, data collection, and original draft preparation; L.W. (Lijie Wu): Conceptualization, methodology, study design, data analysis, data interpretation, reviewing and editing; Y.P.: Funding acquisition, data collection, and data analysis. All authors have read and agreed to the published version of the manuscript.

Funding: National Natural Science Foundation of China (62305262). Natural Science Foundation of Shaanxi Province (2022JQ-652). The project of talent introduction of Xi'an University of architecture and technology (1960320034). Shaanxi Fundamental Science Research Project for Mathematics and Physics (22JSQ026).

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

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Article **Evaluation of Sputtering Processes in Strontium Iridate Thin Films**

Víctor Fuentes¹, Lluis Balcells¹, Zorica Konstantinović², Benjamín Martínez¹ and Alberto Pomar^{1,*}

Instituto de Ciencia de Materiales de Barcelona, ICMAB-CSIC, Campus Universitario UAB,

08193 Bellaterra, Spain; vfuentes@icmab.es (V.F.); balcells@icmab.es (L.B.); benjamin@icmab.es (B.M.)

- Center for Solid State Physics and New Materials, Institute of Physics Belgrade, University of Belgrade, Pregrevica 118, 11080 Belgrade, Serbia
- Correspondence: apomar@icmab.es

Abstract: The growth of epitaxial thin films from the Ruddlesden-Popper series of strontium iridates by magnetron sputtering is analyzed. It was found that, even using a non-stoichiometric target, the films formed under various conditions were consistently of the perovskite-like $n = \infty$ SrIrO₃ phase, with no evidence of other RP series phases. A detailed inspection of the temperature-oxygen phase diagram underscored that kinetics mechanisms prevail over thermodynamics considerations. The analysis of the angular distribution of sputtered iridium and strontium species indicated clearly different spatial distribution patterns. Additionally, significant backsputtering was detected at elevated temperatures. Thus, it is assumed that the interplay between these two kinetic phenomena is at the origin of the preferential nucleation of the SrIrO₃ phase. In addition, strategies for controlling cation stoichiometry off-axis have also been explored. Finally, the long-term stability of the films has been demonstrated.

Keywords: spin-orbit coupling; epitaxial thin films; complex oxides; growth mechanisms; magnetron sputtering

1. Introduction

Oxide thin films, with their unique properties and versatility, stand as catalysts in the pursuit of transformative solutions for electronic and energy applications [1,2]. In addition to the inherent tunability of the physical properties of these oxides in their bulk form, thin film allows the design of emerging functionalities through engineering defect structures, interfaces or even new phase stabilization [3,4]. This last strategy, named epitaxial stabilization, is a versatile tool that has been widely used to enlarge the range and capabilities of functional materials [5]. Taking advantage of the large non-equilibrium conditions used in physical vapor deposition techniques, such as, for example, pulsed laser deposition or magnetron sputtering, oxide thin films of thermodynamically unstable phases have been successfully grown. Furthermore, kinetic effects can be enhanced with the right choice of a substrate that superimposes an additional surface energy to the delicate balance required for grain nucleation [3]. A very-well-studied example in the last years corresponds to the Ruddlesden-Popper (RP) iridates. Each member of the RP family $(Sr_{n+1}Ir_nO_{3n+1})$ is a superlattice of n perovskite layers ($SrIrO_3$) separated by rock salt layers (SrO). The presence of heavy 5d iridium atoms gives rise to a strong spin-orbit coupling (~0.5 eV) that is comparable to electronic correlations [6]. As a consequence, a plethora of interesting aspects in physics has been observed, as the electronic properties range from insulating states for the n = 1 (Sr₂IrO₄) or n = 2 (Sr₃Ir₂O₇) phases to the semi-metallic behavior of the $n = \infty$ (SrIrO₃) phase. Of particular interest is the case of perovskite-like SrIrO₃ (SIO-113) in what follows), which, being close to a metal-insulator transition, has been suggested as a potential candidate for neuromorphic [7] or catalytic [8] applications or as an active ingredient in resistive-based memories [9,10]. Furthermore, the literature about unexpected

Citation: Fuentes, V.; Balcells, L.; Konstantinović, Z.: Martínez, B.: Pomar, A. Evaluation of Sputtering Processes in Strontium Iridate Thin Films. Nanomaterials 2024, 14, 242. https://doi.org/10.3390/ nano14030242

Academic Editors: Jose Maria De Teresa, Ricardo Lopez Anton and Sion Federico Olive Méndez

Received: 30 December 2023 Revised: 19 January 2024 Accepted: 20 January 2024 Published: 23 January 2024



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SIO-113 electronic properties, including strange metallicity [11,12] or the anomalous or topological Hall effect, is large [13–15]. On the other hand, due to its large spin-orbit coupling, it has also been employed in heterostructures for spin torque or spin-to-charge conversion experiments [16–20].

From the point of view of thin-film growth, SIO-113 is a fascinating case in the RP family; while in bulk form, the orthorhombic perovskite phase only stabilizes at high pressures (the stable phase at ambient pressures being hexagonal) [21-23], in the thin-film form it has been routinely synthesized on different substrates. This epitaxially stabilized phase is usually treated as a pseudo-cubic structure with a cell parameter of ~3.95 Å. However, it is known that the complex superlattice structure of RP phases (with the alternating perovskite-rock salt stacking) makes the occurrence of secondary phase intergrowths a real challenge for controlling cation stoichiometry and film disorder. Early works have demonstrated that, by using pulsed laser deposition (PLD), thin films of different RP phases $(n = 1, n = 2 \text{ and } n = \infty)$ can be grown using the very same single target, just by adjusting thermodynamic conditions (oxygen pressure and temperature) during deposition [24–26]. It should be noted that, in those works, several stoichiometric target compositions were used (n = 1 and n = ∞), leading to similar results. In contrast, reports on films grown by magnetron sputtering are scarce. Nevertheless, the few existing reports show that the $n = \infty$ phase is always obtained, even when using off-stoichiometric targets, with no signs of other RP members [9,10,15,27,28]. These results evidence that kinetic effects during growth, even those that are ignored sometimes, should be taken into consideration when analyzing epitaxial growth and stability. Research on this topic is vital because the sputtering process has intrinsic benefits over PLD for a wide area of development and scalability up to industrial capabilities.

In this study, we present a novel analysis of the growth behavior of epitaxial SIO-113 thin films fabricated via magnetron sputtering. Our results uncover a remarkable tendency for the perovskite-like phase to nucleate, contrary to traditional thermodynamic predictions. By conducting thorough microstructural examinations, we make evident for the first time the pivotal role of backsputtering processes and the angular distribution of sputtered species in SIO-113 growth. This research provides a unique understanding of how these factors interact to explain the observed phenomena, presenting valuable insights for future improvements in this field.

2. Materials and Methods

2.1. Film Growth

Epitaxially stabilized perovskite-like SrIrO₃ films have been prepared by using RF magnetron sputtering on top of (001)-SrTiO₃ (STO) single crystalline substrates from a non-stoichiometric iridate target [9]. Details of target preparation are described in the Supplementary Materials. Films were deposited in the range of RT-900 °C in a pure oxygen atmosphere between 6 and 140 mTorr. STO substrates were treated before deposition in order to achieve atomically smooth surfaces of TiO₂ terraces [9]. The course of treatment involved a 10 min ultrasonic leaching in deionized water and a 2 h annealing at 1000 °C [29]. X-ray reflectometry (Siemens D-5000 diffractometer) was used to determine the thickness of SIO-113 samples and to calibrate the growth rate. The SIO films' thickness used in this work were in the range of 20–30 nm.

2.2. Structural and Physical Characterization

Further X-ray measurements were used to evaluate the structural properties of the SIO-113 films. Phase purity was determined from standard θ –2 θ diffraction patterns (Siemens D-5000, Aubery, TX, USA), while reciprocal space maps around (103) peaks were recorded by using a Bruker D8-Discover diffractometer (Bruker, Billeria, MA, USA) to assess the epitaxial quality and orientation of the films.

The surface quality of the samples was studied with atomic force microscopy (MFP-3D AFM Asylum Research, Goleta, CA, USA). Topographic images were recorded in tapping

mode by using Sb-doped Si probes (NCHV-A from Bruker, Billeria, MA, USA). The surface roughness was calculated from the images as a root mean square (rms) of the height distribution. Cation stoichiometry was analyzed by electron probe microanalysis with commercial JXA-8230 equipment from JEOL (JEOL Ltd., Tokyo, Japan). X-ray photoelectron spectroscopy (XPS) measurements were performed with Phoibos 150 equipment from SPECS (SPECS, Berlin, Germany). To preclude the possible presence of contaminants, an overview scan in the range from 0 to 1380 eV was performed firstly. Afterwards, the most relevant peaks were studied in detail to obtain information about the surface composition. In general, these peaks were 3d-strontium, 4f-iridium, 1s-carbon, 1s-oxygen and 2p-titanium. To determine the films' stoichiometry, measurements were taken at different areas of the sample. From these experimental deviations, we estimate an average error of 15% in the determination of the stoichiometric ratio of metallic cations.

The temperature dependence of the resistivity was measured by using a standard four-probe configuration in a PPMS system from Quantum Design between 10 K and 300 K during warming (3 K/min). Measurements were performed along a [100] crystallographic axis in 400 μ m long \times 100 μ m wide tracks patterned by UV lithography and physical etching. Metallic Pt contacts were deposited by sputtering through a suitable shadow mask, and then samples were contacted by using aluminum wire. Electrical current was kept below 50 μ A in all the measurements to avoid local heating.

3. Results and Discussion

3.1. Influence of Growth Conditions

Achieving high-quality stoichiometric oxide films typically requires precise adjustments in the growth conditions. The most straightforward method involves studying the temperature–oxygen phase diagram to pinpoint the specific zone where the preferred oxide phase is thermodynamically favored. In pursuit of this objective, we conducted the growth of a sequence of strontium iridate thin films. These films were grown at various nominal substrate temperatures spanning from 500 °C to 900 °C (the maximum operational temperature within our system) and under oxygen partial pressures ranging between 6 mTorr and 140 mTorr. Films were evaluated by studying their surface roughness and X-ray diffraction patterns. Figure 1 shows the impact of the growth temperature on the microstructure of the films.



Figure 1. Top panels: AFM surface images. **Bottom** panels: X-ray diffraction patterns. **Right** panel: evolution of rms roughness of a series of SrIrO₃ thin films deposited at different temperatures and oxygen pressure of 140 mTorr.

The AFM images in Figure 1 (top row) expose a clear evolution from a flat film at 500 °C to a rough film at 700 °C and then a progressive flattening of the surface up to 900 °C. This roughness evolution may be tracked in the right panel of Figure 1. The RMS roughness reached a minimum value below 0.2 nm, making it appropriate for applications with stringent interfacial quality requirements. At the lowest growth temperature of 500 °C,

only diffraction peaks corresponding to the STO substrate were detected, thus indicating the absence of epitaxial iridate films (see bottom panels in Figure 1). With increasing T, a diffraction peak develops that can be easily identified as the (002) reflection of the perovskite-like $n = \alpha$ SIO-113 phase [15,23]. The peak intensity rises with the growth temperature, indicating enhanced crystallinity. A small shift in the peak was observed that may be attributed to slight differences in oxygen content between the samples. The temperature-dependent evolution of the film's microstructure suggests that the primary effect of the growth temperature is to boost the diffusion of adatoms on the substrate surface, thereby promoting a layer-by-layer growth mechanism.

A similar trend was observed when varying the background oxygen partial pressure during growth (see the Supplementary Materials). It is believed that higher oxygen pressures promote more collisions between species, leading to a better thermalization of the atoms and decreasing the growth rate [15,30]. Unexpectedly, in our case, the thickness of the films has no significant dependence on background pressure. X-ray diffraction patterns (see Figure S2 in the Supplementary Materials) again evidence the exclusive formation of the n = \propto SIO-113 phase as only 00l peaks of this phase have been observed. Its position at 20 = 44.75° corresponds to an out-of-plane cell parameter (assuming pseudocubic phase) c = 0.405 nm. Reciprocal space maps (not shown, see Ref. [9]) confirmed that, in the range of thickness studied in this work, SIO films are always fully strained with the STO underlying substrate (a_{STO} = 0.3905 nm) [9,10,20]. The observed cell parameters point towards an elastic behavior solely attributed to the in-plane compressive strain imposed by the substrate, consistent with prior reports [9].

Our results in Figure 1 suggest that, in spite of the non-stoichiometry of the target, sputtering processes favor the nucleation of the perovskite-like phase of strontium iridate. We have not been able to find any region in the temperature-oxygen phase diagram where n = 1 or where any other Ruddlesden–Popper phase could be identified (from X-ray experiments). These findings are in clear contrast to those reported by other groups using different growth methods. For example, it was demonstrated early that just by modifying thermodynamic growth conditions for different film phases, including the n = 1 phase, Sr₂IrO₄ could be grown from the very same single target [24,25]. In those works, the perovskite-like $n = \infty$ phase just occurred at the low temperature region of the phase diagram with a crossover towards the n = 1 phase when temperature was raised (at 100 mTorr mixing of phases is observed as low as 700 $^{\circ}$ C) [24]. It is noteworthy to mention that, in our scenario, additional experiments involving different background atmospheres, such as a mixture of argon and oxygen to maintain a low oxygen partial pressure while keeping the total pressure constant, resulted in phase segregation and the emergence of metallic iridium at the film surface [8]. In order to elucidate this deviation in our experiments from the commonly reported findings in the literature and gain insights into the various nucleation processes, a more detailed study is thus deserved.

3.2. Film Stoichiometry

Since films are grown from a non-stoichiometric (strontium-rich) target, it is natural to analyze first the stoichiometry of the films. A usual technique to verify the final film composition is microprobe measurements. However, as film and substrate have two elements in common, oxygen and strontium, it is difficult to extract reliable information from the measurements. For this reason, we have grown some samples on top of NGO (NdGaO₃) substrates under the same conditions. The X-ray diffraction patterns were equal to those obtained from STO, thus suggesting that, even if chemistry and cell parameters are different, the SIO-113 growth process could be considered similar. Microprobe experiments showed that there is an excess of strontium in relation to iridium in the films with an atomic relationship close to [Sr]/[Ir] = 1.3 (we should remind readers that the nominal target ratio is 2). Since our focus lies on understanding this cationic relationship, employing X-ray photoelectron spectroscopy (XPS) emerges as a suitable method for gaining deeper insights [31]. Our approach involved a set of XPS experiments crafted to unveil the

stoichiometric distribution across the film's depth. Initially, distinct square regions on a uniform film were delineated via photolithography. These selected areas were subsequently subjected to ion milling with varying durations while maintaining a consistent attack rate. Following this, the depth of the milled regions was measured using AFM profiling to establish the ion milling rate (0.2 nm/s in our case). Then, a full SIO-113 film was etched at successive increased times. After each milling process, XPS experiments were performed to obtain information on the stoichiometry profile. The results are presented in Figure 2.



Figure 2. XPS percentage atomic profile of the different ions present in the SrIrO₃ films. Data are represented as a function of the film thickness from the interphase with the substrate.

As it can be observed in the graph, the atomic oxygen (blue triangles) takes values around 60% for the whole film as well as for the substrate, which is in good agreement with the nominal value in perovskites. On the other hand, strontium cations (red circles) seem to have a higher concentration at the surface of the film (>25%), and after the first nanometers they decay to a constant value slightly above the nominal 20%. Since both the film and the substrate have the same nominal value for Sr, once the interphase is crossed, the Atomic% of the Sr remains constant. Iridium cations (black squares) represent only the 13% of the atoms at the surface, compensating in this way for the overpopulation of Sr. Beyond the surface, the value of the Ir cations increases and it is stabilized at values of 16-19% through the main part of the thickness, which is slightly below the nominal value. Close to the interface with the substrate, iridium starts to decrease smoothly first. At the same time, the titanium signal slowly starts to rise, indicating that any possible interdiffussion is limited to the very first atomic layers of the films. However, we should note that the XPS-probed volume extends to a certain depth and that Ti signals may appear even before the whole $SrIrO_3$ film has been etched. Thus, the interface quality can not be precisely assessed from these experiments. In summary, films exhibit a constant cationic ratio through most of their bulk volume while being strontium-rich (iridium-deficient) close to the free surface. By integrating the whole profile, an overall cationic ratio of [Sr]/[Ir] = 1.30 has been obtained, in very good agreement with the above microprobe measurements of SIO films grown on NGO substrates. Since no titanium diffuses into the bulk of the film beyond the initial layers, the existence of a certain quantity of iridium vacancies could be inferred.

3.3. Sputtering Processes

Physical vapor deposition techniques involve processes of a non-equilibrium nature. It is a fact that cation composition could be affected by kinetic growth mechanisms during the transfer of materials from a multielement target as previously observed also in PLD films [25,26,32]. Thus, to understand the results from the precedent section, we have concentrated on two possible mechanisms that may influence cation stoichiometry. First, we will focus on backsputtered processes and then we will analyze the angular distributions of sputtered atoms.

3.3.1. Backsputtering Phenomenon

It is known that energetic O^{2-} particles generated in the plasma bombard the growing film, causing the reemission of adatoms, therefore reducing their sticking probabilities [4,30]. This backsputtering phenomena may strongly modify the final cation composition and several processing parameters as source power or target distance play an important role in controlling it. We will, however, focus our interest on the less studied role of substrate temperature. Note that other mechanisms, such as, for example, different flight times for the various atomic species, are also important in the amount of material that lands on the substrate surface. However, as there is no way to discriminate between all those processes, for the sake of simplicity, we are just referring to them under the general term of backsputtering.

Figure 3 depicts the changes in thickness and cation composition of the sputtered iridate films obtained from an identical target when deposited at different substrate temperatures by PLD (black) and by sputtering (orange). Figure 3 evidences that PLD and sputtered films follow completely different trends when the temperature of the substrate is increased. On one hand, PLD films do not show any clear correlation between temperature and thickness (Figure 3a) as the observed small fluctuations may be attributed to experimental variability. In contrast, films deposited by magnetron sputtering clearly show a reduction in thickness as temperature is increased. It is worth mentioning that films deposited at 900 $^{\circ}$ C are nearly an order of magnitude thinner than films deposited at room temperature. As the experiments were performed under identical working target-tosubstrate distance and power source, this huge difference in deposited material can only be attributed to backsputtering processes. This implies that, in sputtering, substrate temperature decreases the binding energy of the adatoms at the surface, and the energy threshold for their reemission is more easily achieved. At a simple glance this phenomenon looks hard to master. Furthermore, the proposition that atomic mass could exert an influence has been substantiated through an examination of the stoichiometry of the deposited films. Figure 3b illustrates that while PLD films accurately mirror the composition of the target in the deposited film, sputtered films exhibit a more notable dependence on this factor. Surprisingly, at low temperatures, films are highly deficient in strontium with [Sr]/[Ir] = 0.5. However, above 700 °C, the cation ratio approaches 1.0, and then it continues to increase up to a maximum of 1.3. This indicates that strontium is very prone to backscattering processes and only the formation of the iridate phase starting at 700 $^{\circ}$ C (from results of Figure 1) helps to stop this loss of strontium. Nevertheless, in the whole range of measured temperatures, the [Sr]/[Ir] ratio never arrives at the nominal value of the target, i.e., [Sr]/[Ir] = 2.



Figure 3. Variations in (**a**) film thickness and (**b**) cation stoichiometry with the nominal substrate temperature for films grown by PLD and sputtering. The iridate films were grown by PLD and sputtering.

3.3.2. Angular Distribution

The other process that may influence the deposited films deals with the anisotropy of the flying atoms once extracted from the target. Given the distinct atomic mass and vapor pressure, it is reasonable to assume that sputtered strontium and iridium cations may exhibit a different angular distribution [26,30,33]. One easy way to study this distribution is to perform off-axis sputtering experiments. In this configuration, the substrate is placed out of the axis of the target. With slight variations in this configuration, off-axis sputtering is a usual technique to achieve high-quality thin films by reducing backsputtering and, in consequence, controlling stoichiometry.

We have grown a series of films at different distances, Δx , from the normal axis of the target, as indicated in the image in Figure 4a. The results of the depositions at room temperature (RT) and at 900 °C are depicted in Figure 4c,d. In Figure 4c, it can be observed that when deposited at RT, the thickness of the film rapidly decreases with Δx . The most relevant variation is found between 0 and 25 mm, where the drop in thickness is almost an order of magnitude. After this, the thickness follows a smooth decrease tendency with Δx . On the other hand, at high temperature (900 °C), the thickness of the films remains constant, and only above 25 mm a reduction in thickness can be observed. Interestingly, beyond 25 mm, both behaviors (at room temperature and at 900 $^{\circ}$ C) appear to converge, with room-temperature films being marginally thicker; however, the overall trend remains consistent for both curves. These findings corroborate our earlier analysis, emphasizing the substantial impact of backsputtering mechanisms on the growth of SIO-113 films. In a very simple model, we may assume that the values obtained at room temperature are a good measure of the material landing at the substrate and the differences observed when growing at higher temperature are mostly due to backsputtering. With this in mind, Figure 4c indicates that when the flux of energetic species is high enough (small Δx , i.e., close to on-axis), backscattering is very important at high temperatures (a huge amount of material is removed from the substrate). On the other hand, when the flux of energetic species is lowered (by moving apart from the on-axis configuration, i.e., high Δx), backsputtering, although still present, is severely reduced. Let us now investigate the influence of off-axis configuration on the cation stoichiometry. Figure 4d shows the dependence of the cation ratio [Sr]/[Ir] as a function of off-axis distance, Δx , for films grown at RT and 900 °C. At room temperature, on-axis films are strongly strontium-deficient (or iridium-rich), as previously commented with a cation ratio of [Sr]/[Ir] = 0.5. This is also true for off-axis films up to $\Delta x \sim 10$ mm. Above that, strontium content monotonically increases to reach the nominal target ratio [Sr]/[Ir] = 2 at around 25 mm. For larger values of Δx , the strontium over iridium ratio continues to rise, up to values of [Sr]/[Ir] = 2.5 around Δx ~30 mm. Some kind of equilibrium is achieved at this distance and compositional ratio is unchanged in the remaining samples. These results may be explained assuming that the angular distribution of the ejected atoms is different for strontium and iridium. Iridiumrich on-axis film suggests that iridium plasma is more concentrated along the on-axis configuration, while strontium-rich films for the extreme off-axis configuration lead to a wider distribution of strontium. The schema of Figure 4b depicts a very simple sketch of the possible angular plasma configurations for both sputtered species. At high temperatures (900 °C), the situation is quite different. On-axis films and up to $\Delta x \sim 20$ mm off-axis films exhibit a constant ratio composition of [Sr]/[Ir] = 1.3. Beyond that specific distance, there is a noticeable shift in stoichiometry, characterized by a clear strontium enrichment. To explain this behavior, it is essential to consider the role of the three underlying mechanisms. First, RT results suggest a different angular distribution of sputtered Sr vs. Ir atoms. Second, backsputtering is more important at high temperatures and could be different for both species. Third, at 900 °C, as the perovskite-like $n = \infty$ phase is formed, there are additional mechanisms for attaching the strontium ions to the substrate. The results in Figure 4d are just evidence of the delicate balance between these effects and the fine-tuning needed to obtain oxide thin films of the right stoichiometry and properties.



Figure 4. (a) Scheme showing the sputtering setup used in this work. Δx measures the displacement from the on-axis target–substrate configuration. (b) Sketch of the angular distribution of the sputtered cationic species. (c) Thickness of the films after 1h of deposition at the same power 20 W at different Δx at room temperature (black dots) and 900 °C (orange dots). (d) Cation composition [Sr]/[Ir] at different Δx from the same samples as in (c).

The iridate films grown using "off-axis" conditions only revealed well-crystalized epitaxial phases when high temperature was employed. Figure 5 shows the X-ray θ -2 θ diffraction patterns obtained for this series. The figure shows that films grown up to 2.4 cm exhibit similar X-ray diffraction patterns with peaks corresponding only to the perovskite $n = \infty$ phase SrIrO₃. In this range, the overall stoichiometry was unchanged, close to [Sr]/[Ir] = 1.3-1.5, and selective nucleation of the perovskite phase followed an identical trend. Small differences in the peak position for samples below 2.4 cm may be attributed to slightly different oxygen content, as in the case of Figure 1. However, for the off-axis ($\Delta x = 4$ cm) sample with a stoichiometric ratio [Sr]/[Ir] = 2.8, the diffraction peak moved from $2\theta = 44.7^{\circ}$ towards $2\theta = 44.1^{\circ}$, still far away from the expected positions of both the n = 1 (Sr₂IrO₄) and n = 2 phases (Sr₃Ir₂O₇). This shifting cannot be only attributed to oxygen vacancies, and, instead, a plausible scenario arises where the strontium excess induces an extra chemical strain that strongly distorts the perovskite phase. Furthermore, given the absence of additional reflections, it is not possible to attribute this peak to any phase other than a considerably distorted $n = \infty$ phase. Therefore, despite having a stoichiometrically sufficient amount of strontium for the growth of another Ruddlesden-Popper phase, epitaxial stabilization takes precedence over alternative growth mechanisms. This results in the nucleation of the $n = \infty$ phase and the accommodation, if needed, of significant variations in stoichiometry (such as an excess of strontium). To fully understand the behavior of strongly off-stoichiometric film grown off-axis, and, in particular, to explore the chemically induced strain in these RP series as a strategy for improved properties [34], a complete microscopic study would be required, which, although interesting, is beyond the scope of this work.



Figure 5. θ–2θ measurements of the iridate films deposited at 900 °C at different off-axis Δx positions.

3.4. Thin-Film Stability

It has been previously reported that strontium iridate films are prone to aging, and the surface is rapidly degraded when in contact with air [35]. This raises a severe concern for their use in several applications relying on surface quality, such as, for example, spintronics. To assess the stability of the films, we have studied the evolution of electrical resistivity over several months. Figure 6 shows the typical results for an as-grown film and after being stored in a low-humidity atmosphere. Figure 6a shows that resistivity remains unaltered after a few months of storage (less than 0.3% of variation). The resistivity of the film exhibits a metallic regime in a wide range of temperature and, at very low temperatures, a small upturn can be observed, with results that are similar to those previously reported [9,36–40]. In addition, the cation composition was verified and found to remain unchanged. Nevertheless, there was an observed progressive alteration in the film's surface over time. Figure 6b,c show the AFM images of the very same film just after growth (b) and after 5 months of storage (c). The initial image captured after growth displays a flat morphology. However, after a span of 5 months, the film undergoes a transformation, becoming uniformly coated with small particles that notably increase the film's roughness. Since the composition of the surface is unaltered with time, these particles probably arise from the atmospheric carbon/organic contamination. However, this degradation is purely superficial and it does not alter the macroscopic measurements or intrinsic properties of the film.



Figure 6. (a) Aging of the temperature dependence of the electrical resistivity of a SrIrO₃ film. Inset shows the dependence on aging time of the room temperature resistivity. (b) AFM image of a SrIrO₃ film just after deposition. (c) AFM image of the same film as in (b) after a period of 5 months. Films were stored under inert atmosphere.

4. Conclusions

The study presents a unique analysis of the growth of Ruddlesden-Popper strontium iridate thin films via magnetron sputtering. In contrast with previous reports, our results make evident the formation of the perovskite-like $n = \infty$ SrIrO₃ phase despite using a nonstoichiometric target. A careful analysis of the cation stoichiometry of the sputtered films as a function of various parameters allows us to demonstrate the existence of remarkably different angular sputter distributions for strontium and iridium atoms, which could be of great relevance for the preparation of Ruddlesden-Popper strontium iridate thin films. Additionally, the study identifies an important backsputtering phenomenon at high temperatures, attributed to reactive oxygen ions. By elucidating the interplay between these mechanisms, our results demonstrate the prevalence of kinetic effects over thermodynamic conditions in sputtering growth, offering new opportunities to control and fine-tune cation stoichiometry in oxide thin films. The stability of the oxide films over extended periods is also demonstrated, underscoring the practical relevance of our findings.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/nano14030242/s1, Figure S1: Target preparation; Figure S2: Influence of oxygen pressure.

Author Contributions: The manuscript was written through the contributions of all authors. All authors have read and agreed to the published version of the manuscript.

Funding: This work has received funding from the "Spanish Ministry of Science and Innovation" through "Severo Ochoa" (CEX2019-000917-S) and "OXISOT" (PID2021-128410OB-I00). Z.K. acknowledges funding provided by the Institute of Physics Belgrade (University of Belgrade, Serbia). This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 101007417, having benefited from the access provided by ICMAB within the framework of the NFFA-Europe Pilot Transnational Access Activity, proposal ID352.

Data Availability Statement: Data are contained within the article and Supplementary Materials.

Acknowledgments: We thank the personnel from CCiTUB (University of Barcelona) and from the Scientific and Technical Services of ICMAB and ICN2 for their help and technical support during measurements.

Conflicts of Interest: The authors declare no conflicts of interest.

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Article Heterojunction Devices Fabricated from Sprayed *n*-Type Ga₂O₃, Combined with Sputtered *p*-Type NiO and Cu₂O

Theodoros Dimopoulos ^{1,*}, Rachmat Adhi Wibowo ¹, Stefan Edinger ¹, Maximilian Wolf ¹ and Thomas Fix ²

- ¹ Energy Conversion and Hydrogen Technologies, Center for Energy, AIT Austrian Institute of Technology, Giefinggasse 2, 1210 Vienna, Austria; rachmat.wibowo@ait.ac.at (R.A.W.); stefan.edinger@ait.ac.at (S.E.); maximilian.wolf@ait.ac.at (M.W.)
- ² ICube Laboratory, Université de Strasbourg and Centre National de la Recherche Scientifique (CNRS), 23 Rue Du Loess, BP 20 CR, F-67037 Cedex 2 Strasbourg, France; tfix@unistra.fr

Correspondence: theodoros.dimopoulos@ait.ac.at

Abstract: This work reports on the properties of heterojunctions consisting of *n*-type Ga₂O₃ layers, deposited using ultrasonic spray pyrolysis at high temperature from water-based solution, combined with *p*-type NiO and Cu₂O counterparts, deposited by radio frequency and reactive, direct-current magnetron sputtering, respectively. After a comprehensive investigation of the properties of the single layers, the fabricated junctions on indium tin oxide (ITO)-coated glass showed high rectification, with an open circuit voltage of 940 mV for Ga₂O₃/Cu₂O and 220 mV for Ga₂O₃/NiO under simulated solar illumination. This demonstrates in praxis the favorable band alignment between the sprayed Ga₂O₃ and Cu₂O, with small conduction band offset, and the large offsets anticipated for both energy bands in the case of Ga₂O₃/NiO. Large differences in the ideality factors between the two types of heterojunctions were observed, suggestive of distinctive properties of the heterointerface. Further, it is shown that the interface between the high-temperature-deposited Ga₂O₃ and the ITO contact does not impede electron transport, opening new possibilities for the design of solar cell and optoelectronic device architectures.

Keywords: cuprous oxide; gallium oxide; nickel oxide; heterojunctions; sputtering; spray pyrolysis; electron transport layers; hole transport layers; solar cells

1. Introduction

By virtue of their versatile, wide-ranging electronic properties, metal oxide semiconductors are indispensable materials for a wide range of devices, including photovoltaic (PV) and photoelectrochemical cells, organic light-emitting diodes (OLEDs) and photodetectors, or power electronics components. They provide functionalities as transparent electrodes, charge-carrier-selective transport or injection layers, as well as light absorbers, depending on their electrical conductivity, work function, and bandgap. Nickel oxide (NiO), a p-type wide bandgap (3.4–3.7 eV) semiconductor, bears a high potential to replace organic hole transport layers in perovskite and organic photovoltaic devices, as elaborated in many recent reviews [1-5]. Cuprous oxide (Cu₂O), also a *p*-type material, with a bandgap of 1.9–2.6 eV, has been introduced as a hole-transport layer in perovskite cells [6], recently achieving very promising efficiency and stability results [7]. Because of its relatively low bandgap, it has been widely investigated as a light absorber in all-oxide solar cells [8], as well as in photoelectrochemical cells for water splitting [9]. Gallium oxide (Ga₂O₃), on the other hand, is an n-type, wide-bandgap (4.8–5.0 eV) semiconductor that has demonstrated high potential in solar cells when combined with Cu₂O, as will be elaborated later. However, it has also found implementation as an electron-transport layer in perovskite solar cells [10]. Heterojunctions between Ga₂O₃ and NiO or Cu₂O are of interest, both from a fundamental and applications points of view.

Citation: Dimopoulos, T.; Wibowo, R.A.; Edinger, S.; Wolf, M.; Fix, T. Heterojunction Devices Fabricated from Sprayed *n*-Type Ga₂O₃, Combined with Sputtered *p*-Type NiO and Cu₂O. *Nanomaterials* **2024**, *14*, 300. https://doi.org/10.3390/ nano14030300

Academic Editor: Zhan'ao Tan

Received: 16 December 2023 Revised: 26 January 2024 Accepted: 27 January 2024 Published: 1 February 2024



Copyright: © 2024 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). Ga_2O_3/NiO junctions have been investigated in the literature, mainly for applications in power electronics, as summarized in a recent review [11]. In these devices, NiO thin films have been deposited on single-crystal Ga_2O_3 substrates or thick (several micrometers) Ga_2O_3 layers [12–15], with different techniques, including sol-gel [12], atomic layer deposition (ALD) [13], and radio-frequency (RF) sputtering [13,14]. The reverse architecture has also been reported: Wang et al. [16] sputter-deposited 4 µm thick films of NiO, combined with sputtered 200 nm thick Ga_2O_3 films, for use as self-powered photodetectors. In all of these works, a type II band alignment at the heterojunction has been shown, with conduction band offset (CBO) between 0.9 and 2.7 eV and valence band offset (VBO) between 2.1 and 3.6 eV [12–17]. This wide spread of values shows the sensitivity of the energy band alignment on the material's processing, crystal orientation, and other factors. However, such thick films cannot be applied as electron and hole transport layers in PV or OLED devices and reducing the thickness to the tens of nanometers regime—or further—is challenging for the structural integrity of the layers and, therefore, the operation of the device.

The interest in Cu_2O/Ga_2O_3 heterojunctions has increased in the last decade, since Minami et al. reported high-efficiency (\sim 5.4%) Cu₂O/Ga₂O₃ solar cells, using thermal oxidation of Cu sheets at high temperatures for the preparation of Cu₂O and pulsed laser deposition for Ga₂O₃. The high efficiency is caused by the optimum conduction band alignment between the p and n layers [18]. A bit later, Lee at al. reported 1.2 V open circuit voltage and efficiency of ~4% in Cu₂O/Ga₂O₃ heterojunctions with electrodeposited Cu₂O and Ga₂O₃ fabricated by ALD, with optimized band alignment and passivation of interface defects [19]. Chua et al. showed that, when growing Ga_2O_3 by ALD on top of Cu₂O grown by chemical vapor deposition (CVD), exposure to air is of vital importance for the transport properties, as a CuO layer forms on the Cu₂O. By avoiding air exposure between the deposition of the two layers, they could enhance the open circuit voltage from 1.4 V to ~1.8 V [20]. From these works, one can conclude that, from the point of view of interface stoichiometry control, it is advantageous to deposit Cu₂O on Ga₂O₃ and not vice versa, unless the surface oxidation of Cu₂O can be avoided. Benz et al. fabricated both oxide layers by sputtering and investigated the VBO and CBO at the interface. They found that α -Ga₂O₃/Cu₂O has the lowest CBO of ~0.2 eV and a VBO of ~3.2 eV, while, in β -Ga₂O₃/Cu₂O junctions, the CBO increases to ~1.3 eV and the VBO to ~3.7 eV. To this respect, they claimed that the use of α -Ga₂O₃ bears the highest potential for application in solar cells in combination with Cu₂O [21]. Their work, however, did not show electrical characterization of the junctions.

The present work reports for the first time the properties of heterojunctions composed of *n*-type Ga_2O_3 layers deposited by ultrasonic spray pyrolysis [22], in combination with RF- and DC-sputtered *p*-type NiO and Cu₂O counterparts, respectively. The structural, optical, and electronic properties of the single layers are investigated before the analysis of the electrical transport characteristics of the junctions in the dark and under simulated solar light, yielding information about the energy band alignment in the two junction types.

2. Materials and Methods

Three types of substrates were used in this study: the first was uncoated borosilicate glass (NEXTERION[®] D, 1.0 mm thickness, cut in 25 × 25 mm size, Schott, Jena, Germany), used for the deposition of Ga₂O₃ by spray-pyrolysis, due to its superior thermal stability. The second was uncoated, soda-lime, microscope slides (size: $25 \times 25 \times 1.0$ mm, Menzel Gläser, Braunschweig, Germany), used for the deposition of the sputtered layers, and the third was ITO-coated glass (size: $25 \times 25 \times 1.1$ mm, Product No. 703192, Merck, Darmstadt, Germany) with a sheet resistance of 8–12 Ω /sq, used for the deposition of devices.

For the patterning of the ITO-coated substrates, the following procedure was followed: polyimide film tape (Kapton[®], DuPont Teijin Films, Chester, VA, USA) with a width of 12.5 mm was used to cover a middle stripe of the ITO, before immersing the substrate into a 9 M HCl aqueous solution (1:1 dilution), etching away the ITO from the uncovered area.

After the etching, the substrate was rinsed with ultrapure water (resistivity: 18 M Ω ·cm, Arium[®], Göttingen, Germany) and the tape was removed. The substrate was then thoroughly cleaned by ultrasonication in a bath with ultrapure water and cleaning concentrate (HelmanexTM III, Merck, Darmstadt, Germany), under sonication at 50 °C, followed by sonication in ultrapure water and, finally in isopropanol (each step for a 15 min duration), before being blown-dry in nitrogen stream. The same cleaning procedure was applied for the bare glass substrates.

The substrates were then transferred to the spray pyrolysis setup (Sono-Tek ExactaCoat[®], equipped with a Sono-Tek Impact[®] ultrasonic nozzle operating at 120 kHz, Sono-Tek Corporation, Milton, NY, USA), where they were heated to 380 °C and coated with Ga₂O₃, following the process described in [22]. The layer thickness range was between 12 and 30 nm. For the Ga₂O₃ deposition on the ITO substrate, a layer thickness of 15 nm was chosen. A 3 mm wide stripe was left uncoated on one side of the ITO substrate to be later used as back-side contact. After the Ga₂O₃ deposition, the substrates were left to cool down to ~50 °C, before being taken off the hotplate. After the spray-pyrolysis, due to the applied thermal budget, the ITO substrate's sheet resistance increased to 51 ± 6 Ω /sq.

For the sputtering, a Leybold Univex cluster tool was used (Leybold, Cologne, Germany). All layers were deposited without substrate heating at a substrate-to-target distance of ~9 cm. The deposition of NiO was carried out using a NiO target (101.6 mm diameter, 99.99% purity, AJA Int., Scituate, MA, USA), mounted on an RF magnetron source. The applied sputter power was 200 W and pure Ar was used as process gas at a pressure of 10 µbar, resulting in a sputter rate of 0.11 nm/s. Layers of 20-40 nm in thickness were deposited. The deposition of Cu₂O was carried out using a metallic Cu target (101.6 mm diameter, 99.995% purity, Materion, Mayfield Heights, OH, USA), mounted on a DC magnetron source. A sputter power of 80 W was applied for the deposition in an atmosphere of $Ar/O_2:80/20$ at a pressure of 10 µbar. Prior to each deposition process, the target was sputtered in pure Ar atmosphere at 120 W and 5 µbar pressure for at least 10 min, followed by 5 min in Ar/O_2 atmosphere at 80 W. This step served to condition and clean the target from the oxide and achieve reproductible deposition results with pure Cu₂O phase. At these conditions, the sputter rate was 0.74 nm/s. The deposition of the device contacts was carried out using an Au target (76 mm diameter, 99.99% purity, Neyco, Vanves, France) at 20 W and 2 µbar Ar pressure, resulting in a rate of 0.8 nm/s. The contacts were sputtered through a shadow mask, defining active device areas of 5.73 mm² and 10.43 mm².

The sputter deposition rates for NiO and Cu₂O were extracted by measuring the layer thickness (step height) using a surface profilometer (Alpha-Step[®] IQ, KLA-Tencor, Milpitas, CA, USA). The morphology of the layers was measured by scanning electron microscopy (SEM) (Zeiss Ultra 40, Zeiss, Oberkochen, Germany) with a beam accelerating voltage of 5 kV and an in-lens detector. The surface topography was evaluated by atomic force microscopy (AFM) (PicoPlus, Molecular Imaging, Tempe, AZ, USA) in tapping mode, using SSS-NCHR probes (NanosensorsTM, Neuchatel, Switzerland). The open-source software Gwyddion, version 2.61, was used to plot and analyze the AFM data. Structural characterization of the layers was realized using a grazing incidence X-ray diffractometer (XRD) (ARL Equinox 100, Thermo Fisher Scientific, Waltham, MA, USA) at an angle of 5 °, with Cu- K_{α} radiation. The analysis of the diffractograms was conducted using the Match! Software, version 3.14 (Crystal Impact, Bonn, Germany), with reference databases from Crystallographic Open Database (COD).

Transmission and reflectance spectra were recorded by a Fourier transform spectrometer (FTS) (Bruker, Billerica, MA, USA, Vertex 70) equipped with a halogen lamp as a source of unpolarized light (64642 HLX, Osram Licht, Munich, Germany). Direct transmittance was measured at normal incidence in reference to air and reflectance was measured at an incidence angle of 13° in reference to a calibrated mirror (STAN-SSH-NIST, Ocean Optics, Orlando, FL, USA). A GaP and a Si diode detector were used for the spectral ranges of 303–588 nm and 500–1205 nm, respectively. Optical simulations were performed using a transfer matrix method (TMM) algorithm, described by Ebner et al. [23]. The sheet resistance was determined using an in-line four-point probe (Nagy SD–600, Nagy Instruments, Gäufelden, Germany). Current density–voltage (*j*-*V*) curves of solar cells were obtained with two-point measurements, using a semiconductor parameter analyzer (4156C, Agilent Technologies, Santa Clare, CA, USA) under dark and AM1.5G-simulated illumination (LOT-Oriel solar simulator, Darmstadt, Germany). For the capacitance–voltage (*C*-*V*) measurements, an LCR Meter was used (4284A, Agilent Technologies, Santa Clare, CA, USA).

For the determination of the work function (WF) and ionization energy (IE) of the layers, Kelvin probe and ambient pressure photoemission spectroscopy (APS) were performed in air (KP Technology, Wick, UK, APS03). A 2 mm diameter Au-coated tip was calibrated using air photoemission. The WF of the material was determined by measuring the contact potential difference between the Kelvin probe tip and the surface of the sample. The IE was measured using the same system by photoelectron emission. Finally, for the electrochemical impedance spectroscopy (EIS), a 3-electrode cell was used, with the coated sample serving as a working electrode, platinized Ti mesh as a counter electrode, and Ag/AgCl as reference. The cell was connected to a potentiostat (Vionic, Metrohm, Herisau, Switzerland). A 0.5 M Na₂SO₄ aqueous electrolyte was used.

3. Results

3.1. AFM and SEM Characterization

AFM characterization was realized for layers deposited on glass substrates. All layers have low roughness, with fine grain structure, making them suitable for implementation in ultra-thin solar cells and optoelectronic devices. The largest roughness is measured for Ga₂O₃: the 30 nm thick layer yields RMS roughness of 2.0 nm (Figure 1a), with the background roughness of the borosilicate glass being 0.3 nm (Figure S1a). The lowest roughness is measured for NiO: the 40 nm thick layer yields RMS roughness of the glass substrate (Figure S1b). The RMS value for the 40 nm thick Cu_2O is 1.6 nm (Figure 1c), with a grain size considerably larger than for Ga₂O₃ and NiO.



Figure 1. AFM images of single layers of: (**a**) $Ga_2O_3(30)$, (**b**) NiO(40), and (**c**) $Cu_2O(40)$, along with the corresponding RMS roughness values.

The heterojunction multilayers also feature low roughness. Figure 2 shows the roughness evolution with the sequential deposition of layers. The ITO back electrode (heated to the temperature used for the Ga_2O_3 deposition, i.e., 380 °C) has an RMS value of 2.2 nm. The deposition of 15 nm Ga_2O_3 atop, leads to a marginal increase in the RMS to 2.4 nm. The RMS further increases moderately with the deposition of the 20 nm NiO, reaching 2.8 nm. On the other hand, 100 nm of Cu_2O brings the RMS to 2.6 nm, increasing to 4.1 nm when a 300 nm Cu_2O film is deposited. The AFM images suggest that, with the increase in Cu_2O thickness, the film acquires a more compact character, which helps to keep the overall roughness of the stack at low levels.



Figure 2. AFM images of the: (a) ITO substrate, (b) ITO/ $Ga_2O_3(15)$, (c) ITO/ $Ga_2O_3(15)$ /NiO(20), (d) ITO/ $Ga_2O_3(15)$ / $Cu_2O(100)$, and (e) ITO/ $Ga_2O_3(15)$ / $Cu_2O(300)$ stacks, along with the obtained RMS roughness values.

The compact character of the layers can be further evidenced in the cross-section SEM images, shown in Figure 3. One can clearly distinguish the ITO layer with a thickness of ~125 nm, followed by the compact and continuous Ga_2O_3 interfacial layer and the NiO, having a combined thickness of ~35 nm (Figure 3a). On the other hand, for the sample in Figure 3b, the Cu₂O layer has a thickness of ~300 nm. The plain-view SEM images (Figure 3c,d) show again very different grain structures between the ultra-thin NiO and the thick Cu₂O.



Figure 3. Cross-section and plain-view SEM images of the (**a**), (**c**) ITO/Ga₂O₃(15)/NiO(20) and (**b**), (**d**) ITO/Ga₂O₃(15)/Cu₂O(300) stacks.

3.2. Structural Characterization

Single NiO and Cu₂O layers of different thicknesses were deposited on plain glass substrates for XRD characterization. As described in [22], relatively thick (>150 nm) spraypyrolyzed Ga₂O₃ layers adopt the monoclinic β -Ga₂O₃ structure, with predominant (111) texturing. However, GIXRD diffractograms of thin films of the order used in this work (15– 30 nm) show no reflection peaks (apart from the broad background of the glass substrate on which they were deposited).

For the NiO layers, down to a thickness of 20 nm, crystalline structure reflections can be observed (Figure 4a). For the 100 nm film, the pattern is composed of the (111), (200), (202), and (311) peaks, with the (200) and (111) being the most prominent, in agreement with the reference for cubic NiO (Fm3m, COD: 96-432-0506). For the 40 nm film, the (200), (111), and (202) peaks are clearly visible and, even for the 20 nm thick film, the (200) peak can still be distinguished. The structure of the RF-sputtered films agree with various reports from the literature implementing DC or RF mode sputtering in Ar and Ar/O₂ atmosphere [24–26].



Figure 4. GIXRD patterns of the (a) NiO and (b) Cu_2O single films of different thicknesses. (c) GIXRD patterns of the ITO, ITO/Ga₂O₃(15), and ITO/Ga₂O₃(15)/Cu₂O(300) stacks.

The Cu₂O 220 nm thick film yields a pattern that perfectly matches the cuprite cubic reference (Pn3m, COD: 96-900-5770), with high-intensity (111), (020), and (202) peaks, underlining the polycrystalline character of the deposit (Figure 4b). Similar results were obtained by reactive DC sputtering of Cu₂O from a Cu target in the literature [27]. A clear pattern is also distinguished for the 40 nm film, with the aforementioned reflections present. For the 20 nm film, no reflections are visible. In conclusion, the GIXRD characterization demonstrates the crystalline nature of the NiO and Cu₂O, as well as the phase purity, as no foreign reflections were detected.

Figure 4c shows the GIXRD pattern of the ITO substrate, corresponding to the cubic structure (Ia³, COD: 96-231-0010). After the deposition of the Ga₂O₃ layer at high temperature, the reflection peaks of the ITO remain unchanged and no additional peaks can be observed. For the complete ITO/Ga₂O₃/Cu₂O(300) multilayer, both In₂O₃ and Cu₂O patterns can be clearly distinguished. The same polycrystalline pattern is obtained for the Cu₂O on the ITO/Ga₂O₃ substrate as on the glass, which is not always the case for sputtered Cu₂O films [28]. It is noted, however, that, in this case, the Cu₂O peaks are all slightly shifted to the right with respect to the reference and the single films, which can be attributed to an induced stress when the layer is deposited on top of the ITO/Ga₂O₃ substrate.

3.3. Optical Characterization

To extract the refractive index from optical spectra, single layers of the oxides with a thickness below 50 nm were deposited to avoid light interference patterns in the spectra that can complicate the index determination procedure. Figure 5a–c show transmittance (*T*), reflectance (*R*), and absorbance (A = 1 - T - R) spectra for the Ga₂O₃(30), NiO(40), and Cu₂O (40) layers, respectively (for Ga₂O₃, A is practically zero). All spectra are referenced

to air. Each graph also includes the *T* and *R* spectra of the glass substrates. The Ga₂O₃ layer is highly transparent over the whole spectrum, while NiO presents considerable absorption losses for wavelengths < 600 nm. In the same spectral region, as expected, Cu₂O presents strong absorption. Considering the refractive index of the glass $n_{\rm G}$ = 1.52 and air as the surrounding medium ($n_{\rm air}$ = 1.00), the transfer matrix method (TMM) was used to calculate the complex refractive index of the materials in the range 400–1000 nm, as shown in Figure 5d–f. Due to the negligible absorption, only the real part of the refractive index is plotted for Ga₂O₃, with *n* decreasing continuously with the wavelength from 1.89 at 400 nm to 1.72 at 1000 nm. The results are in line with the literature reports for Ga₂O₃ layers fabricated by different techniques like sputtering [29] or plasma-enhanced atomic layer deposition [30].



Figure 5. Transmittance (*T*), reflectance (*R*), and absorbance (*A*) spectra for single layers of (**a**) $Ga_2O_3(30)$, (**b**) NiO(40), and (**c**) $Cu_2O(40)$, together with the *T* and *R* of the respective glass substrates. The second row shows the calculated refractive index and extinction coefficient for (**d**) Ga_2O_3 , (**e**) NiO, and (**f**) Cu_2O .

A significantly larger *n* is calculated for NiO, decreasing from 2.57 at 400 nm to 2.42 at 1000 nm. The extinction coefficient κ decreases with the wavelength from $\kappa = 0.14$ at 400 nm to 0.017. Likewise, the refractive index of the NiO layer agrees with literature results from spectroscopic ellipsometry measurements of reactively sputtered NiO films [31]. For Cu₂O, *n* maximizes to the value of 3.79 at 450 nm and reaches a plateau at 2.79 above 700 nm. The extinction coefficient has the value of 1.00 at 400 nm, dropping to 0.055 for $\lambda > 600$ nm. The extracted complex refractive index of Cu₂O agrees very well with reported values for bulk material measured by spectroscopic ellipsometry [32], indicating the high optical quality of the sputtered films.

The bandgap of the sprayed Ga_2O_3 was previously reported to be ~5.0 eV [22]. Here, the bandgap values of NiO and Cu₂O are calculated from the optical spectra of thicker films (Figure 6a,b), using the Tauc plot method [33]. For this, the absorption coefficient is obtained from the relation [34]:

$$\alpha = \frac{1}{t} \ln \left(\frac{1 - R}{T} \right)$$

where *t* is the film thickness. The relation $(\alpha h\nu)^m = C(h\nu - E_g)$ is used to fit the linear part of the plot $(\alpha h\nu)^m$ vs. $h\nu$, corresponding to the band-edge of the material. The factor *m* assumes the value of 2 for direct bandgap, 1/2 for indirect bandgap, and 2/3 for direct forbidden transition.



Figure 6. Transmittance, reflectance, and absorbance (A = 1 - T - R) spectra for (**a**) NiO(100) and (**b**) Cu₂O(220) layers. (**c**) Tauc plots for the bandgap estimation of the NiO and Cu₂O layers, assuming direct and direct forbidden transition for Cu₂O and direct transition for NiO. Also shown are the linear fits in the band-edge regions (red lines).

For NiO (Figure 6c), the best linear fit of the band edge is obtained for m = 2 (direct bandgap), giving rise to a bandgap value of 3.41 eV. This value is at the low end of the reported literature range for sputtered NiO films, which is 3.34–3.71 [24,35–37]. For Cu₂O (Figure 6c), an equally satisfactory linear fit in the band-edge region can be obtained if a direct allowed (m = 2) or direct forbidden (m = 2/3) transition is considered, with the latter being a more realistic assumption for this material [38]. In both cases, the bandgap value is $E_g = 2.54$ eV, as can be seen in Figure 6c. This value is in the upper end of the range reported for Cu₂O layers, prepared by sputtering, which is between 2.18 and 2.58 eV [39–41]. A general conclusion in the literature is that the widening of the Cu₂O bandgap relates to the reduction in defects and enhanced crystallization, which were achieved with the help of annealing [40,41] or the use of mixed O₂-N₂ reactive gas during deposition [39].

Figure 7 shows optical spectra for the heterojunctions at sequential stages of their deposition. Interestingly, the transmittance of the glass/ITO substrate that is coated with the Ga₂O₃(15) layer is higher than the transmittance of the uncoated ITO (subjected to the thermal stress of the spray deposition). This is due to a reduction in the reflectance losses, as seen from the comparison of the two reflectance spectra in Figure 7. The deposition of the NiO(20) on the Ga₂O₃ reduces considerably the transmittance for λ < 620 nm due to the absorption of the NiO layer. The transmittance after the deposition of 100 nm Cu₂O shows enhanced absorption for λ < 470 nm and a subsequent gradual increase in the *T* as the band edge of the material is approached.



Figure 7. Transmittance, reflectance, and absorbance spectra for the heterojunctions at sequential stages of their deposition.

3.4. Electronic Properties Characterization

The Kelvin probe measurements yielded work function (WF) values of 4.8, 4.9, and 4.2 eV for Cu₂O, NiO, and Ga₂O₃, respectively. The WF for Ga₂O₃ is 0.7 eV higher than the one previously extracted from UPS measurements [22]. It is known, however, that the two techniques give rise to distinctive values, as UPS measurements take place in ultra-high vacuum and Kelvin probe in air. Furthermore, the former gives a minimum value of the WF (as it is estimated by comparing the Fermi energy and the low-energy cut-off of the secondary electrons), while the latter gives an average over the probed electrode area. In addition, as pointed out in the introduction, the air-exposed surface of Cu₂O is covered with an atomically thin layer of CuO, which has a smaller WF than Cu₂O [42]. For this reason, the extracted value is only representative of the air-exposed Cu₂O but not of the surface formed upon Cu₂O deposition on Ga₂O₃ under vacuum. The ionization energy (IE) values, extracted from APS measurements, are 5.2 eV for both Cu₂O and NiO samples. For the Ga₂O₃, the IE cannot be extracted from the APS, as it is below the measurable limit.

From the EIS measurements, at a frequency of f = 1 kHz, Mott–Schottky plots were constructed (Figure 8), showing negative slopes and, therefore, *p*-type conductivity for both Cu₂O and NiO layers. The hole carrier density *N* was extracted from the formula:

$$N = \frac{2}{qA^2\varepsilon_0\varepsilon\cdot S}$$

where *q* is the electron charge, *A* the electrode area in the electrolyte, ε_0 the vacuum permittivity, ε the permittivity of the semiconductor (7.6 for Cu₂O and 11.9 for NiO) [43], and *S* the slope of the linear fit of the Mott–Schottky plot. Carrier density values of $5.2 \times 10^{24} \text{ m}^{-3}$ and $8.0 \times 10^{24} \text{ m}^{-3}$ for Cu₂O and NiO, respectively, were extracted, as shown in Figure 8a,b, respectively. These high carrier density values are in agreement with other works in the literature on sputtered Cu₂O [44] and NiO [31] films.



Figure 8. Mott–Schottky plots for the (a) $ITO/Cu_2O(200)$ and (b) ITO/NiO(40) samples. The red lines are linear fits.

3.5. Heterojunction Charaterization

For the heterojunctions, a standard Ga₂O₃ thickness of 15 nm was selected, based on an initial screening of the thickness-dependent performance, described in the Supplementary Information (Figure S2).

The properties of the ITO/Ga₂O₃(15)/NiO(20)/Au(100) heterojunctions were analyzed under dark and illuminated conditions. For a typical device, dark and illuminated *j*-*V* curves are shown in Figure 9a in a semilogarithmic scale (inset shows photo of a sample). The dark *j*-*V* shows large rectification (>1000 at |V| = 0.5 V), which demonstrates the formation of a high-quality *n*/*p* junction between the ultra-thin Ga₂O₃ and NiO layers. The dark *j*-*V* shows a low turn-on bias of ~30 mV in the forward direction (positive bias applied on the Au contact). The ideality factor *n* of the junction can be extracted from the fitting of the *j*-*V* curve for intermediate forward bias, in the range 0.16–0.36 V, using the diode equation:

$$j = j_0 \cdot \exp\left[\frac{qV}{nkT}\right]$$

which is derived as an approximation for the intermediate bias region of the general equation:

$$j = j_0 \cdot \left\{ \exp\left[\frac{q\left(V - j \cdot R_S^*\right)}{nkT}\right] - 1 \right\} + \frac{V - j \cdot R_S^*}{R_P^*}$$

where j_0 is the saturation current density, $R_S^* = R_S \cdot A$ and $R_P^* = R_P \cdot A$, with R_S and R_P being the series and the parallel resistance, respectively, and A the junction area, k the Boltzmann constant, and T the temperature. The first term in the above equation corresponds to the exponential diode current, whereas the second term is the shunt current, which can be approximated as V/R_p^p for reverse and low forward bias. The average ideality factor and standard deviation over five devices is $n = 1.6 \pm 0.2$. The ideality factor is, therefore, as expected from the Sah-Noyce-Shockley theory [45], in the regime between 1 and 2. The Ga_2O_3 /NiO junction is a wide-gap, type II heterojunction with a large CB offset and an even larger VB offset. These large offsets block currents, so interface recombination is regarded as the dominant carrier transport channel across the heterojunction. The temperature dependence of the dark j-V characteristics was measured at 25, 40, 50, 60, 70, and 80 °C and the results are shown in Figure 9b. From the fitting in the intermediate forward voltage range, it is obtained that the ideality factor only slightly decreases with increasing temperature, as expected for the generation-recombination type of carrier transport. For the device shown in Figure 9, n decreases from 1.4 at ambient temperature to 1.3 at 80 °C (Figure 9b, f). From the fitting of the dark *j*-V curves in the region (-0.2, 0.1) V, a high parallel resistance is extracted, with a value of 11.7 M Ω cm² (Figure 9b). For all measured NiO solar cells, the parallel resistance was in the M Ω cm² range at ambient temperature. The illuminated curves show a very low short-circuit current





Figure 9. (a) *j*-*V* curves in dark and under illumination for the Ga₂O₃(15)/NiO(20) junction together with a photo of a sample. (b) Dark *j*-*V* curves of the Ga₂O₃(15)/NiO(20), as a function of the temperature, with the fitting for ideality factor and parallel resistance for T = 25 °C and 80 °C. (c) *j*-*V* curves in dark and under illumination for the Ga₂O₃(15)/Cu₂O(300) junction together with a photo of a sample. (d) Dark *j*-*V* curves of the Ga₂O₃(15)/Cu₂O(300), as a function of the temperature, with the fitting for ideality factor and parallel resistance for T = 25 °C and 80 °C. (e) Plot of the parallel resistance of the devices as a function of the temperature. (f) Plot of the ideality factor of the devices as a function of the temperature.

The *j*-*V* characteristics of the Cu₂O-based heterojunctions were also analyzed in a similar manner. In Figure 9c,d, typical curves for the ITO/Ga₂O₃(15)/Cu₂O(300)/Au(100) stack under dark and illuminated conditions are plotted in a semilogarithmic scale (inset shows photo of a sample). The dark *j*-*V* shows large rectification at much higher bias than

for the NiO junctions (>1000 at |V| = 2 V). A low parallel resistance dominates the junction properties at low and intermediate bias regimes. From the fitting of the *j*-V curves in the regime (-0.5, 0.5) V, a parallel resistance of 108 k Ω cm² is extracted at ambient temperature. For all solar cells of this type, the R_P was in the range 60–170 k Ω cm².

Parallel current can be caused by the trapping and de-trapping of the carriers at defect states in the space charge region of the device. These defects can act either as recombination centers or traps depending upon the relative capture sections of the electrons and holes [46]. When charges entering the space charge region are captured in these states, they can further jump from one state to the other through tunneling or being thermally re-emitted into the conduction or valence band or to another such state. These mechanisms contribute to the R_P , while the recombination mechanism contributes to the exponential term in the current. The thermal (re)emission from the traps depends on the temperature as, with increasing temperature, the rate of trap depopulation is increased, giving rise to more free carriers. This process is described by the equation:

$$dN_t(T) = -N_t(T)v \exp\left(-\frac{E}{kT}\right)dt,$$

where $N_t(T)$ is the number of trapped carriers at temperature *T*, *E* the energy of the state, and ν the attempt-to-escape frequency, which is proportional to the density of states of the conduction or valence band, the capture cross-section of electrons or holes, and their thermal velocity. As elaborated in [46], this process leads to an ohmic behavior of the shunt current with respect to the bias voltage and an exponential dependence with respect to the temperature. This agrees with the observed exponential dependence of the parallel resistance on the temperature for both types of solar cells, as shown in Figure 9e.

Another important characteristic of the Cu_2O heterojunction *j*-V curves is the high ideality factors (>3.5) obtained in the exponential current growth regime. In this case, the ideality factor shows a moderate increase from 3.7 at ambient temperature to 4.0 at 80 °C, as can be seen from Figure 9f. Such high ideality factors were reported for inorganic [47–49], organic [50], and perovskite devices [51] and have been attributed to different origins, such as (a) the existence of other rectifying junctions in the stack, (b) shunts and defects, especially at the borders of the junction areas, (c) transport across tunnel barrier, or (d) energy state disorder. Rectifying junctions can be, indeed, formed at either contact: ITO/Ga_2O_3 or Cu_2O/Au . A rectifying ITO/Ga₂O₃ junction cannot be responsible for the large ideality factor, as this would also influence the ideality factor of the heterojunctions employing NiO, which, as shown before, is not the case. A Schottky junction between Cu₂O and Au is also not probable in view of the favorable energy band alignment. However, to exclude this possibility, heterojunctions with a NiO(20) layer inserted between the Cu₂O and Au were deposited. The NiO/Au contact should be ohmic, as the Ga_2O_3/NiO junctions have low ideality factors. However, the junctions with the inserted NiO have also shown ideality factors in the same range as the ones without NiO (Figure S3). From these experiments it can be concluded that contact-related rectifying junctions cannot be at the origin of the high ideality factors. Edge shunts related to the device fabrication can contribute to increasing the ideality factor; however, they would be expected to influence similarly both heterojunctions with NiO and Cu₂O, which is not the case. The ideality factor increases with decreasing Cu₂O thickness and the concomitant decrease in the device shunt resistance, as can be seen in the dark *j*-V curves of Figure S4 for devices with 100 and 50 nm thick Cu₂O. The main contribution to the large ideality factor is assumed to arise from the field-assisted recombination current at the Ga_2O_3/Cu_2O interface due to the lowering of the potential barrier of traps or trap-assisted tunnelling at defect levels in the depletion region. With the increase in the forward bias, the electric field at the depletion region is reduced, decreasing these current contributions, which translates into an increased ideality factor [52,53].

Another important conclusion from the j-V characterization of the heterojunctions is that the ITO/Ga₂O₃ junction should have a low energy barrier for electrons to explain the observed transport characteristics. This is in contradiction to the measured large WF

difference between ITO and Ga₂O₃ (0.6 eV), which should lead to a blocking of the electron transport and to very low currents. The question therefore arises regarding the reason for the observed unimpeded transport characteristics. An explanation is based on a significant amount of work in the literature on the type of contact between ITO and β -Ga₂O₃. Carey et al. reported ohmic contact between an *n*-type β -Ga₂O₃ wafer, with a carrier concentration of $\sim 3 \times 10^{17}$ cm⁻³, and Ti/Au, through an intermediate 10 nm thick, sputtered ITO layer. While Ga₂O₃/Ti/Au contacts remained of Schottky type after thermal rapid annealing at 600 °C, Ga₂O₃/ITO/Ti/Au contacts showed ohmic characteristics after annealing at 500 °C, dramatically improving the electron transport across the heterointerface [54]. The creation of an ohmic contact was attributed to the interdiffusion of In, Sn, and Ga at the heterojunction. Xia et al. [55] showed the reaction of sputtered ITO with highly doped Ga_2O_3 at temperatures > 300 °C. TEM and EDX characterization showed a roughening of the heterointerface, associated with the presence of a wide reaction zone, where the In and Sn from the ITO diffuse into the Ga₂O₃, with a corresponding modification of the electrical junction characteristics. The reaction zone significantly increased after annealing at 400 °C, with the interface losing its integrity at 500 °C. These results are aligned with the present work, showing an unimpeded electron transport at the ITO/Ga_2O_3 interface, suggesting a low potential barrier for electrons. An intermixed interface is highly probable in view of the high substrate temperature used for the spray pyrolysis of Ga₂O₃ on ITO (380 °C) applied for the deposition duration of ~15 min but also the extended cooling-down phase, with ~15 min needed for the sample to reach 250 $^{\circ}$ C.

To gain more insight on the involved heterointerfaces, *C*-*V* measurements were realized for the NiO and Cu₂O devices, using the parallel capacitance, C_P , and parallel conductance, G_P , equivalent circuit. The measured capacitance and conductance, C_M and G_M , were corrected for the series resistance, R_S , using the approach described in [56,57]. The R_S is calculated from the capacitance and conductance values at strong accumulation ($C_{M, acc}$, $G_{M, acc}$) using the equation:

$$R_S = \frac{G_{M, acc}}{G_{M, acc}^2 + \omega^2 C_{M, acc}^2}$$

The C_p and G_p in the three-element model are calculated by the following equations:

$$C_P = \frac{\left(G_M^2 + \omega^2 C_M^2\right) \cdot C_M}{\alpha^2 + \omega^2 C_M^2}$$
$$G_P = \frac{\left(G_M^2 + \omega^2 C_M^2\right) \cdot \alpha}{\alpha^2 + \omega^2 C_M^2}$$
$$\alpha = G_M - \left(G_M^2 + \omega^2 C_M^2\right) \cdot R_S$$

Based on the above approach, the Mott–Schottky plots $\left(\frac{A}{C_P}\right)^2$ vs. *V* for the NiO and Cu₂O junctions and for f = 10 kHz are shown in Figure 10a,b, respectively. The plots show a distinct linear region that corresponds to junction depletion. From the fit and extrapolation of the linear portion of the plots, the built-in potential, V_{bi} , can be extracted, which is ~0.8 V for the NiO junction and ~1.8 V for Cu₂O. The qV_{bi} corresponds to the difference in the Fermi levels between the *n* and *p* sides of the junction. The value of 0.8 eV is not far from the WF difference between Ga₂O₃ and NiO found from the Kelvin probe measurements, while the 1.8 eV is much larger than the WF difference between Ga₂O₃ and Cu₂O from the Kelvin probe. However, as mentioned before, the formation of a CuO surface layer does not allow the estimation of the correct WF of Cu₂O by the Kelvin probe. So, the value of ~6.0 eV extracted from the Mott–Schottky plot, considering the 4.2 eV as the WF of Ga₂O₃, is assumed to be a representative WF value for the Cu₂O layer.



Figure 10. Mott–Schottky plots for (**a**) the $Ga_2O_3(15)/NiO(20)$ junction and (**b**) the $Ga_2O_3(15)/Cu_2O(300)$ junction (red lines are linear fits), together with the corresponding band diagrams, showing the anticipated CBO and VBO in both cases.

4. Conclusions

In conclusion, it was shown that high-quality *n*-Ga₂O₃, *p*-NiO and *p*-Cu₂O layers can be deposited by spray-pyrolysis (Ga_2O_3) at high temperature and RF (NiO) and reactive DC sputtering (Cu₂O) without substrate heating, with properties that make them suitable as electron- and hole-transport layers, respectively, in different types of solar cells, such as perovskite and organic, as well as optoelectronic devices. Type II heterojunctions are formed between the Ga₂O₃ and NiO or Cu₂O. Ga₂O₃/NiO junctions show large offsets for both conduction and valence bands, while, for Ga₂O₃/Cu₂O, a large offset is only present for the valence band. The rectification is high for both types of junctions. Their transport characteristics can be described by a generation-recombination channel in the first case, with an ideality factor between 1 and 2, while, in the second case, high ideality factors above 3.5 suggest significant contributions from field-assisted recombination at increased trap density in the depletion region. Further, it was shown that a low resistance ITO/Ga_2O_3 contact is formed that does not hinder electron transport, despite the expectations from the band structure of the individual layers. This is assumed to be due to the interface intermixing during the high-temperature deposition of Ga₂O₃. Low resistance contacts to Ga₂O₃ are of interest for power electronic devices, apart from the applications aforementioned. Open circuit voltage values of ~220 and ~940 mV were achieved for the NiO- and Cu₂O-based junctions, respectively. Ga_2O_3/NiO junctions absorb only in the UV region and can be applicable as photodiodes or transparent image sensors. Visible-active solar cells can be based on the Ga₂O₃/Cu₂O heterojunction. At the current state, the short circuit current is too low for practical implementation but the optimization of the absorber thickness, as well as its structural and electronic properties (e.g., grain size and charge carrier mobility) can lead to significant improvements in performance.

Supplementary Materials: The following supporting information can be downloaded at: https: //www.mdpi.com/article/10.3390/nano14030300/s1, Figure S1: AFM images of the glass substrates; Figure S2: Initial screening of the effect of Ga₂O₃ thickness on the open circuit voltage, realized for samples with a Ga₂O₃ thickness gradient; Figure S3: *j*-*V* curve of heterojunction with inserted NiO layer between Cu₂O and Au; Figure S4: *j*-*V* curves of heterojunctions with reduced Cu₂O thickness.

Author Contributions: Conceptualization, T.D.; Formal Analysis, T.D., R.A.W., S.E., M.W. and T.F.; Investigation, T.D., R.A.W., S.E., M.W. and T.F.; Writing—Original Draft Preparation, T.D.; Writing— Review and Editing, T.D., R.A.W., S.E., M.W. and T.F; Visualization, T.D. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the European Union, through the Horizon Europe project SUNREY.

Data Availability Statement: Data are contained within the article and Supplementary Material.

Conflicts of Interest: The authors declare no conflicts of interest.

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Article Synthesized PANI/CeO2 Nanocomposite Films for Enhanced **Anti-Corrosion Performance**

Ahmad M. Alsaad ^{1,*}, Mohannad Al-Hmoud ², Taha M. Rababah ³, Mohammad W. Marashdeh ², Mamduh J. Aljaafreh², Sharif Abu Alrub², Ayed Binzowaimil² and Ahmad Telfah^{4,5}

- 1 Department of Physics, Jordan University of Science and Technology, P.O. Box 3030, Irbid 22110, Jordan 2
- Department of Physics, College of Science, Imam Mohammad Ibn Saud Islamic University (IMSIU), P.O. Box 90950, Riyadh 11623, Saudi Arabia; mmalhmoud@imamu.edu.sa (M.A.-H.); mwmarashdeh@imamu.edu.sa (M.W.M.); maljaafreh@imamu.edu.sa (M.J.A.); snabualrub@imamu.sa (S.A.A.); ambinzowaimil@imamu.edu.sa (A.B.)
- 3 Department of Nutrition and Food Technology, Faculty of Agriculture, Jordan University of Science and Technology, P.O. Box 3030, Irbid 22110, Jordan; trababah@just.edu.jo
- 4 Department of Physics, University of Nebraska at Omaha, Omaha, NE 68182, USA; a.telfah@ju.edu.jo
- 5 Nanotechnology Center, The University of Jordan, Amman 11942, Jordan
- Correspondence: alsaad11@just.edu.jo or amalsaad@unomaha.edu; Tel.: +962-2-720100 (ext. 23422); Fax: +962-2-7201071

Abstract: This study introduces a novel nanocomposite coating composed of PANI/CeO2 nanocomposite films, aimed at addressing corrosion protection needs. Analysis through FTIR spectra and XRD patterns confirms the successful formation of the nanocomposite films. Notably, the PANI/CeO2 nanocomposite films exhibit a hydrophilic nature. The bandgap energy of the PANI composite film is measured to be 3.74 eV, while the introduction of CeO₂ NPs into the PANI matrix reduces the bandgap energy to 3.67 eV. Furthermore, the electrical conductivity of the PANI composite film is observed to be $0.40 \text{ S} \cdot \text{cm}^{-1}$, with the incorporation of CeO₂ NPs leading to an increase in electrical conductivity to 1.07 S·cm⁻¹. To evaluate its efficacy, electrochemical measurements were conducted to assess the corrosion protection performance. Results indicate a high protection efficiency of 92.25% for the PANI/CeO₂ nanocomposite film.

Keywords: corrosion protection; protonated polyaniline (PANI); cerium dioxide (CeO₂); optical bandgap energy; electrical conductivity

1. Introduction

Corrosion of metals has been one of the essential problems that faces scientific and industrial societies. Corrosion exerts significant economic and environmental consequences across several divisions of worldwide infrastructure and metal-based properties. Beyond risking public security and prompting considerable destruction, deterioration dislocates operations, dictating wide-ranging asset renovation and replacement. Universally, erosion perpetrates over USD 2.5 trillion in compensations annually, corresponding to 3.4% of the global gross domestic product (GDP) [1,2]. There is a lot of consideration from these societies to improve long-life corrosion protection coating [3,4]. Plans for corrosion inhibition comprehend miscellaneous tactics, including proper design, engagement of corrosion-inhabitant alloys, application of anticorrosion coatings, use of corrosion inhibitors, adoption of cathodic fortification techniques, anodic passivation methods, salt removal procedures, and regular cleaning practices [5,6]. Amongst these methods, anticorrosion coatings are accounted as an efficient, versatile, cost-effective, and up-front solution. Remarkably, industries in China assign 66.5% of their corrosion prevention budget towards anticorrosion coatings, underscoring their prominence [7].

Anticorrosion coatings offer twofold approaches for fortification of materials. First, they offer passive protection by acting as physical barriers in contrast to corrosive agents,

Citation: Alsaad, A.M.; Al-Hmoud, M.; Rababah, T.M.; Marashdeh, M.W.; Aljaafreh, M.J.; Abu Alrub, S.; Binzowaimil, A.; Telfah, A. Synthesized PANI/CeO₂ Nanocomposite Films for Enhanced Anti-Corrosion Performance. Nanomaterials 2024, 14, 526. https:// doi.org/10.3390/nano14060526

Academic Editors: Jose Maria De Teresa, Ricardo Lopez Anton and Sion Federico Olive Méndez

Received: 13 February 2024 Revised: 8 March 2024 Accepted: 8 March 2024 Published: 15 March 2024



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illustrated by polymeric dyes and Al₂O₃ coatings [8,9]. The barrier characteristics and ionic response of these coatings analytically impact their corrosion protection efficacy [10–12]. However, passive protection's operational effectiveness depends on the coating's physical integrity, which does not warranty optimum substrate protection. Corrosive agents can infiltrate intact coatings through pores, free volumes, and channels, attaining the substrate surface. Secondly, anticorrosion coatings provide an energetic shield by integrating corrosion inhibitors or compensating materials into their preparations to hinder or halt corrosion. Examples include zinc-rich coatings and smart coatings, capable of safeguarding the substrate metal post-damage [13]

Polyaniline (PANI) is one of the most promising conductive polymers that is used in the fabrication of corrosion protective coating due to its good redox recyclability, variable electrical conductivity, and good environmental stability [14]. PANI nanocomposites are used as an exhilarating technique to enhance the corrosion protection performance significantly. This could be attributed to the fact that PANI composite coating triggers the redox action in an extensive range of pH values and increases corrosion protection performance [15–17].

Several works have elaborated on techniques to enhance the corrosion protection of PANI coating by introducing ceria nanoparticles (CeO₂ NPs) [18]. M. Hosseini and K. Aboutalebi [19] reported that incorporating epoxy coating with CeO₂@PANI@MBT significantly enhances the corrosion protection performance of mild steel substrates. In addition, M. Montemor et al. [20] and L. Calado et al. [21] reported that modifying silane film and siloxane film by CeO₂NPs enhances the corrosion protection and film stability. Y. Lei et al. [22] concluded that PANI/CeO₂ nanocomposite coating could be a potential candidate to improve the protection performance of the epoxy coating on carbon steel.

In this research, we introduce an innovative nanocomposite coating comprising PANI/CeO₂ nanocomposite films tailored for corrosion protection applications. We delve into a comprehensive analysis of the chemical, structural, morphological, and surface wettability properties of these PANI/CeO₂ nanocomposite films. Furthermore, we explore the impact of incorporating CeO₂ into the PANI matrix on the thermal stability of the composite. Detailed investigations into the optical and electrical properties, including absorption coefficient, bandgap energy, and electrical conductivity, provide valuable insights. Additionally, we conduct a thorough examination of the corrosion protection performance of PANI/CeO₂ nanocomposite films across varying temperatures, shedding light on their efficacy in real-world conditions.

2. Corrosion Protection

2.1. Corrosion Mechanism

Corrosion signifies the procedure whereby metals undertake chemical or electrochemical reactions with their surroundings, leading to their conversion into more chemically stable oxides. This phenomenon contains the electrochemical oxidation of metals in reaction with various oxidants, such as oxygen, hydrogen, or hydroxide. Corrosion formation, demonstrated by the creation of iron oxides, assists as a conspicuous sketch of electrochemical corrosion, classically categorized by the occurrence of a distinctive orange hue. The detrimental effects of corrosion spread to the dilapidation of the material and structural properties, covering mechanical strength, appearance, and resistance to the pervasion of liquids and gases [23]. The corrosion susceptibility of structural alloys is often delicate with contact to atmospheric moisture, although this process can be expressively influenced by the existence of specific substances. Corrosion manifestations may range from localized concentrations, resulting in colliery or fissure formation, to more diffuse, unchanging degradation across the surface. Given that corrosion is primarily a diffusion-driven phenomenon, it mainly takes place on exposed surfaces. Accordingly, techniques intended at weakening the activity of uncovered surfaces, such as passivation and chromate conversion, serve to enlarge a material's resistance to corrosion [24].

From a chemical standpoint, corrosion can be explicated as an electrochemical process wherein oxidation occurs at a distinct location on the metal surface, functioning as the anode. Electrons injected at this anodic site traverse through the metal to an alternative location on the object, where reduction of oxygen occurs, expedited by the manifestation of hydrogen ions (H⁺). These hydrogen ions may originate from carbonic acid (H₂CO₃), shaped through the dissolution of carbon dioxide from the ambient air into water under moist atmospheric circumstances. Otherwise, hydrogen ions in water may originate from the dissolution of other acidic oxides existent in the atmosphere, thus raising cathodic behavior at this site [25].

Galvanic corrosion is displayed when two dissimilar metals launch either physical or electrical contact with one another within a communal electrolytic environment or when a singular metal is opened to electrolytes with fluctuating concentrations. In a galvanic couple, the metal with greater reactivity (the anode) practices accelerated corrosion, while the more inert metal (the cathode) undergoes corrosion at a slower rate. Equally, when immersed independently, each metal corrodes at its own pace. Assortment of suitable metals can be channeled by reference to the galvanic series. For instance, zinc frequently obliges as a sacrificial anode for safeguarding steel structures [26].

2.2. Corrosion Prevention Mechanism

The shielding tools engaged by anticorrosion coatings encompass diverse strategies, such as the effects of the type of the coating, reticence, inactiveness, and self-healing. Barrier coatings are aided by impeding the ingress of corrosive agents to the substrate, while coatings comprising zinc or its alloys confer cathodic protection. Furthermore, anodic chemical treatment is achievable for coatings responsive to passivation processes [27]. Another category, intelligent or smart coatings, is designed to selectively release reparative or protective agents to damaged areas upon external stimulus, ensuring active and durable deterioration prevention for the coated metal [28–30].

2.3. Anticorrosion Coatings

Three main types exist: mineral, inorganic, and organic coatings. Metallic coatings can function as barriers and offer cathodic protection by experiencing galvanic corrosion, depending on their nobility in relation to the base metal [31]. Collective procedures for utilizing the above three mentioned coatings include thermal dropping, silver-plating, hot spurting, shielding, biochemical gas exposure, and superficial amendment using focused energy (laser or ion) rays [5,32].

Inorganic coatings primarily safeguard the implemented substrate via blockade prevention mechanisms; however, using Zn-based coatings enhances cathodic fortification [33]. This class comprises various materials such as hydraulic adhesives, ceramic ware, muds, crystal, carbon, and silicon-based coatings. Chemical alteration coatings, which transform the metal surface into a passive film, improve the corrosion protection enactment, making them active bases for subsequent protective paint applications [32]. The sol-gel derived coatings reveal excellent barrier capability. On the other hand, sol-gel coatings composed of a hybrid mixture of organic and certain inorganic materials offer enhanced performance due to their tractability, corrosion safeguard, and applicable curing condition [34–39]. Progressions in the field include the incorporation of graphene, renowned for its waterproofness to corrosive agents and limitation of moisture and ion diffusion, thus stimulating coatings against corrosion [40]. Mixtures of organic–inorganic preparations, predominantly organic–inorganic nanocomposites, have established amplified linkage to substrates, raised thermal stability, and fortified barrier properties, extending the durability of coated materials in perplexing scenarios [41].

The deliberate addition of nanoparticles, bridging metal oxides, clay minerals, and carbonbased materials has suggestively heightened the traits of organic coatings. Nanoparticleinfused coatings unveil perceptible improvements in mechanical strength, barrier physical appearance, and UV resistance, so refining inclusive enactment and protective efficacy across miscellaneous environments [42].

3. Methods

3.1. Materials

The samples used in this study were prepared from the following materials: Polyaniline (PANI, emeraldine base, 50,000 g/mol), camphor sulfonic acid (CSA, 232.30 g/mol), N-Methyl-2-Pyrrolidone (NMP, 99.133 g/mol), ferric oxide nanoparticles (Fe₃O₄NPs, 50–100 nm particle size), cerium dioxide nanoparticles (CeO₂NPs of size less than 50 nm). All the materials were purchased from Sigma Aldrich (formally Millipore Sigma, St. Louis, MO, USA).

3.2. Synthesis Technique

To prepare the PANI composite solution, 0.5 g Polyaniline and 0.12 g CSA were dissolved in 100 mL NMP. The mixture was subjected to vigorous magnetic stirring overnight at 55 °C. To obtain a homogenous solution, the PANI composite solution was sonicated at 55 °C for three hours. Moreover, solution mixed method was utilized to synthesize PANI/CeO₂ NPs nanocomposite solutions. Under magnetic stirring for 5 h, 5 wt.% of CeO₂ was added separately to the PANI composite solution at room temperature.

The resulting PANI/CeO₂ nanocomposite solutions were sonicated for 3 h at room temperature. To obtain the desired investigated structures, we employed the casting technique to deposit PANI and PANI/CeO₂ nanocomposite films on ITO and steel substrates. The casting process was conducted under ambient conditions, specifically at room temperature and ambient atmospheric pressure. To prevent any modifications on the surface morphology and to ensure complete drying of all residuals, the deposited films were dried at 40 °C under ambient conditions overnight.

3.3. Characterization Methods

The chemical, structural, and morphological characterizations were conducted using an FTIR microscope (HYPERION 3000 Bruker), XRD (Malvern Panalytical Ltd., Malvern, UK), and SEM micrographs (Quanta FEG 450), respectively. Thermogravimetric analysis (TGA, NETZSCH) was utilized to investigate the thermal stability of the as-prepared PANI and PANI/CeO₂ thin films. A UV–Vis spectrophotometer (Hitachi U-3900H) with a total internal sphere was used to obtain and interpret the optical properties. A four-point probe (Microworld Inc., Farmington Hills, MI, USA) hocked up to a high-resolution Keithley 2450 Sourcemeter was employed to measure and interpret the electrical conductivity. The corrosion protection performance was investigated using the polarization method. The contact angle measurement was performed utilizing a custom-built setup comprising a commercial camera focused on the stage within the confocal distance. This experimental arrangement involved capturing images of the pendant drop, with the camera connected to a computer for data acquisition and digitization. A syringe positioned in front of the camera was used to generate a pendant drop suspended from a metallic needle. This description has also been integrated into this manuscript.

4. Results and Discussion

The chemical, structural, and morphological characteristics of PANI and PANI/CeO₂ nanocomposite films were investigated and interpreted using the FTIR absorbance spectra (Figure 1), XRD patterns (Figure 2), as well as SEM and water contact angle measurements (Figure 3). Figure 1 displays the FTIR spectra of PANI and PANI/CeO₂ nanocomposite films in the 500–4000 cm⁻¹ spectral range. For the protonated PANI film, the C=N iminoquinone vibrational band appears at 660 cm⁻¹ [23]. Additionally, the absorption band at 825 cm⁻¹ is assigned to the aromatic rings. This is strong evidence of the formation of the polymer [24]. The vibrational band that appears at 950 cm⁻¹ refers to the $-SO_3H$ group, ratifying the PANI protonation with CSA. Furthermore, the in-plane C–H bending vibrations within the quinoid unit (N=Q=N) appear at 1125 cm⁻¹. Also, the aromatic

C–N stretching vibrations appear in the 1300–1500 cm⁻¹ spectral range [25]. The C–N stretching vibrations inside benzenoid (N–B–N) and quinoid (N=Q=N) rings are located at 1541 and 1651 cm⁻¹, respectively. The absorption bands beyond 3000 cm⁻¹ indicate the N–H stretching vibrations [25]. Incorporation of CeO₂ NPs into the protonated PANI films strongly moved the vibrational bands to a higher region of the spectrum. This strong shift is mainly attributed to the difference in the electronegativity between CeO₂ NPs and the PANI molecules.



Figure 1. The FTIR spectra of PANI and PANI/CeO₂ nanocomposite films in the 500–4000 cm⁻¹ spectral range.

Figure 2 shows the XRD patterns of PANI and PANI/CeO₂ nanocomposite films in the $10^{\circ}-50^{\circ}$ angular range. The crystal structure of PANI is mainly determined by the synthesis conditions and the type of the protonic acid [26]. The protonated PANI film shows diffraction peaks at 14.97°, 20.72°, and 25.38° corresponding to (011), (001), and (110) diffraction crystallographic planes [27]. Additionally, a diffraction peak located at 27.86° is associated with the CSA, confirming the protonation of PANI. The semi-crystalline protonated PANI with CSA has two phases, namely, the phase in which the polymer chains are ordered (crystalline phase) and the phase in which the polymer chains are randomly distributed (amorphous phase) [28]. On the contrary, the protonated PANI/CeO₂ nanocomposite film exhibits an amorphous phase.



Figure 2. The XRD patterns of PANI and PANI/CeO₂ nanocomposite films in a diffraction angle range of 10° – 50° .

Figure 3 demonstrates the 1 μ m scaled SEM micrographs and water contact angle (WCA) measurements for PANI and PANI/CeO₂ nanocomposite films. As evident from the observation, the protonated PANI film exhibits a rod-like structure with a water contact angle (WCA) of 38°, suggesting its hydrophilic nature (Figure 3a). This characteristic is known to influence corrosion [29]. Adding CeO₂ NPs into the PANI matrix leads to the decrease of the grain sizes as well as the WCA (24°) (Figure 3b).



Figure 3. SEM images of (a) PANI and (b) PANI/CeO₂ nanocomposite films at 1 µm scale.

The absorption spectra of PANI and PANI/CeO₂ nanocomposite films were investigated. The absorption coefficient can be expressed as $\alpha = (1/d)\ln((1-R)/T)$ [30,31]. The parameters *T*, *R*, and *d* stands for the transmittance, reflectance, and film thickness, respectively. The parameter α exhibits a sudden decrease from 0.01 to 0.003 as the incident wavelength increases from 300 to 350 nm. Beyond $\lambda = 350$ nm, it attains a constant value as demonstrated by Figure 4. The vibration band that appears between 400 and 480 nm is related to the superposition of the π - π * transition within the benzoin ring with the confined polaron (polaron- π *) transition [32]. Introducing CeO₂ NPs into the PANI composite matrix increases α in the visible region and shifts the absorption edge into the red region. The bandgap energy of both PANI and PANI/CeO₂ nanocomposite films was calculated based on the Tauc plot [33,34]. The bandgap energy of the PANI composite film was calculated to be 3.74 eV. Introducing CeO₂ NPs into the PANI matrix decreases the bandgap energy to 3.67 eV.



Figure 4. Absorption coefficient spectra of PANI and PANI/CeO₂ nanocomposite films.

Both PANI and PANI/CeO2 nanocomposite films were electrically characterized by measuring their electrical conductivity using a four-point probe at 12 distinct points. The measured electrical conductivity of the PANI composite film was determined to be $0.40 \text{ S} \cdot \text{cm}^{-1}$. This value falls within the range typically reported for HCl protonated polyaniline films, which typically exhibit conductivities ranging from 1.9 to 3.5 S cm⁻¹ [35]. Additionally, the data reported in Ref. [36] corroborates this finding. In this study, the PANI-CSA film exhibited a similar electrical conductivity of 0.40 S·cm⁻¹. The crystallographic structure of PANI promotes interactions between neighboring polarons, facilitating interchain transitions and enhancing polaron delocalization along the polymer chain. This structural conformation also optimizes the packing of polymer chains into a highly ordered molecular state, thereby favoring higher electrical conductivity compared to localized configurations [25]. This structural conformation also optimizes the packing of polymer chains into a highly ordered molecular state, thereby favoring higher electrical conductivity compared to localized configurations. The high conductivity observed can be attributed to the strong acid-doping of CSA, which introduces additional charge carriers by protonating the imine nitrogen of the PANI backbone [37]. The incorporation of CeO_2 NPs into the PANI composite film results in a more than twofold increase in electrical conductivity, reaching $1.07 \,\mathrm{S} \cdot \mathrm{cm}^{-1}$. To gain further insight into the electrical conductivity values, electrical conductivity maps (1 cm \times 1 cm) of PANI and PANI/CeO₂ nanocomposite films were generated and are presented in Figure 5. Analysis of Figure 5a shows significant conductivity variation across the PANI composite film, attributed to substantial surface morphology alterations and variations in the quality and conditions of the growth process. The introduction of CeO₂ NPs into the PANI composite matrix induces notable changes in the conductivity distribution, likely due to the dispersion of nanoparticles within the PANI matrix (Figure 5b).



Figure 5. The electrical conductivity maps of (a) PANI and (b) PANI/CeO₂ nanocomposite films.

The polarization method was used to elucidate the corrosion rate of PANI and PANI/CeO₂ nanocomposite films. The corrosion test was evaluated in 3.5 wt.% NaCl solution at a temperature of 298 K (Figure 6a). The corrosion potential (E_{corr}) and corrosion current (I_{corr}) were evaluated at the junction where the tangent of the anodic and cathodic polarization curves intersects. The corrosion rate of the nanocomposite films can be calculated using $CR = kMI_{corr}/\rho_m$ [38,39], where k is a parameter equal to 3268.5 mol/A, M stands for the molecular weight of carbon steel, and ρ_m is the density of carbon steel. The parameters E_{corr} , I_{corr} , and CR of electrochemical measurements are tabulated in Table 1. The corrosion rate of PANI-coated carbon steel is lower than the corrosion rate of bare carbon. In addition, incorporating PANI with CeO₂ decreases the corrosion rate. The lowest corrosion rate is found for PANI/CeO₂ nanocomposite films (0.112 mm/year). The protection efficiency ($\eta_{PROT}(\%)$) can be calculated using $\eta_{PROT}(\%) = (i_{corr}^0 - i_{cort}^{coat})/i_{corr}^0 \times 100\%$, where

the parameter i_{corr}^0 represents the corrosion current of bare carbon steel and i_{corr}^{coar} stands for the corrosion current of the nanocomposite-coated carbon steel [40]. The higher protection efficiency was obtained for PANI/CeO₂ nanocomposite films with a value of 92.25%.



Figure 6. (a) Tafel curve of carbon steel coated with PANI and PANI/CeO₂ nanocomposite films at 298 K, (b) corrosion rate of carbon steel coated with PANI and PANI/CeO₂ nanocomposite films as a function of temperature [K], and (c) corrosion rate of carbon steel coated with PANI and PANI/CeO₂ nanocomposite films as a function of 1000/temperature [K] fitted to Arrhenius function.

Table 1. Electrochemical parameters values for carbon steel coated with PANI and PANI/CeO₂ nanocomposite films at 298 K values calculated from Tafel plots.

	C-Steel	PANI	PANI/CeO ₂
CR [mm/year]	1.445	0.390	0.112
η_{PROT} (%)	-	72.90	92.25
E_a [eV]	0.27	0.34	0.39

The corrosion rates of PANI and PANI/CeO₂ nanocomposite films were calculated in the 298–338 K temperature range (Figure 6b). As the temperature of the electrochemical reaction is increased, the corrosion rate for all nanocomposite films increases. This increase is a direct consequence of the enhanced electrochemical reaction rates as well as the increase in the kinetic energy of the molecules in the electrolyte solution. Therefore, the diffusion rate of the molecules is significantly increased. To clarify the thermal activated processes of the corrosion reactions [41], the corrosion rates of PANI and PANI/CeO₂ nanocomposite films versus the reciprocal of temperature (1000/T[K]) are illustrated in Figure 6c. As can be seen, corrosion rates exhibit Arrhenius-like behavior ($CR = CR_0 \exp(-E_a/K_BT)$) [42]. This means that the corrosion rate of bare carbon steel and carbon steel coating by PANI, PANI/ZrO₂, PANI/Fe₃O₄, and PANI/(ZrO₂-Fe₃O₄) nanocomposite films are thermally activated. The activation energies deduced by Arrhenius fitting are tabulated in Table 1. Obviously, the highest activation energy is obtained for the PANI/CeO₂ nanocomposite film. Thus, the effect of temperature on the corrosion rate of the PANI/CeO₂ nanocomposite film is more pronounced than for other investigated samples.

Figure 7 illustrates the effect of coating on the Nyquist and the Bode plots of PANI and PANI/CeO₂ nanocomposite films immersed in 3.5 wt.% NaCl at 298 K. In the Nyquist plot, the curves have single capacity arcs with large radii for PANI/CeO₂ nanocomposite films compared to bare carbon steel and PANI film (Figure 7a), indicating the resistance of these nanocomposites as very high. The coating has an exceptional physical barrier influence on the electrolyte. The impedance value (Z) depicted in the Bode diagram at a frequency of 0.1 Hz demonstrates an increase from 652 $\Omega \cdot cm^{-2}$ for the bare steel to 1900 $\Omega \cdot cm^{-2}$ for the PANI/CeO₂ nanocomposite film. Additionally, for the PANI/CeO₂ film, the impedance



value is recorded at 1930 $\Omega \cdot \text{cm}^{-2}$. Thus, coating the carbon steel with the PANI/CeO₂ nanocomposite film enhances the corrosion resistance (Figure 7b).

Figure 7. (a) Nyquist and (b) Bode plots of carbon steel coated with PANI and PANI/CeO₂ nanocomposite films at 298 K.

5. Conclusions

This work reports the results of a novel nanocomposite coating of PANI/CeO₂ nanocomposite film for corrosion protection applications. FTIR spectra and XRD patterns confirm the formation of the nanocomposite films. Water contact angle measurements confirm that the PANI/CeO₂ nanocomposite film has a hydrophilic nature. Therefore, the films can interact with water through hydrogen bonding. Optical measurements reveal that the bandgap energy of the PANI composite film is 3.74 eV. Introducing CeO₂ NPs into the PANI matrix decreases the bandgap energy to 3.67 eV. Consequently, bandgap engineering in the PANI/CeO₂ nanocomposite film could be a powerful technique for the design of new materials and devices based on this novel material. In addition, band diagrams with continuous bandgap variations can be generated in heterojunctions designed from this novel material and fabricated using techniques such as molecular beam epitaxy. The electrical conductivity measurements reveal that the PANI composite film exhibits an electrical conductivity of 0.40 S·cm⁻¹. Introducing CeO₂ NPs into the PANI composite film increases the electrical conductivity by more than twofold to $1.07 \text{ S} \cdot \text{cm}^{-1}$. The corrosion protection performance was investigated using electrochemical measurements. The protection efficiency of the PANI/CeO₂ nanocomposite film is 92.25%. In general, the efficiency of an inhibitor increases with an increase in the inhibitor concentration. Obtaining excellent inhabitation for incorporating 5 wt.% of CeO₂ in PANI nanocomposite films is very promising for corrosion protection applications.

Author Contributions: Conceptualization: A.M.A., M.A.-H. and A.T.; methodology: A.M.A., M.A.-H., M.W.M. and A.T.; investigation: A.M.A., M.A.-H., T.M.R., M.W.M., M.J.A., S.A.A., A.B. and A.T.; data curation: A.M.A., M.A.-H., T.M.R., M.W.M., M.J.A., S.A.A., A.B. and A.T.; formal analysis: A.M.A., M.A.-H. and A.T.; writing—original draft: A.M.A., M.A.-H., T.M.R., M.W.M., M.J.A., S.A.A., A.B. and A.T.; writing—original draft: A.M.A., M.A.-H., T.M.R., M.W.M., M.J.A., S.A.A., A.B. and A.T.; funding acquisition: A.M.A. and M.A.-H.; project administration: A.M.A. and M.A.-H.; resources: A.M.A., M.A.-H., T.M.R., M.W.M., M.J.A., S.A.A., A.B. and A.T.; funding acquisition: A.M.A. and M.A.-H.; project administration: A.M.A. and M.A.-H.; resources: A.M.A., M.A.-H., T.M.R., M.W.M., M.J.A., S.A.A., A.B. and A.T.; validation: A.M.A., M.A.-H., T.M.R., M.W.M., M.J.A., S.A.A., A.B. and A.T.; validation: A.M.A., M.A.-H., T.M.R., M.W.M., M.J.A., S.A.A., A.B. and A.T.; validation: A.M.A., M.A.-H., T.M.R., M.W.M., M.J.A., S.A.A., A.B. and A.T.; validation: A.M.A., M.A.-H., T.M.R., M.W.M., M.J.A., S.A.A., A.B. and A.T.; validation: A.M.A., M.A.-H., T.M.R., M.W.M., M.J.A., S.A.A., A.B. and A.T.; validation: A.M.A., M.A.-H., T.M.R., M.W.M., M.J.A., S.A.A., A.B. and A.T.; validation: A.M.A., M.A.-H., T.M.R., M.W.M., M.J.A., S.A.A., A.B. and A.T.; validation: A.M.A., M.A.-H., T.M.R., M.W.M., M.J.A., S.A.A., A.B. and A.T.; validation: A.M.A., M.A.-H., T.M.R., M.W.M., M.J.A., S.A.A., A.B. and A.T. and agreed to the published version of the manuscript.

Funding: This research project is funded by the Deanship of Scientific Research at Imam Mohammad Ibn Saud Islamic University (IMSIU) (grant number IMSIU-RP23104).

Data Availability Statement: The data that support the findings of this study are available on request from the corresponding author [Ahmad Alsaad]. Unprocessed data are available upon request from the corresponding author.

Conflicts of Interest: The authors declare no conflicts of interest.

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Review Using Deep Eutectic Solvent-Assisted Plating Baths to Electrodeposit Composite Coatings: A Review

Vyacheslav Protsenko

Ukrainian State University of Chemical Technology, Nauky Ave., 8, 49005 Dnipro, Ukraine; vprotsenko7@gmail.com; Tel.: +380-567753804

Abstract: This review provides a systematic analysis of the literature data on the electrodeposition of composite coatings using plating baths based on a new generation of room-temperature ionic liquids known as deep eutectic solvents (DESs). Such systems offer several advantages over traditionally used aqueous electrolytes and organic solvent-based electrolytes. The colloidal–chemical properties of suspension and colloidal electrolytes for composite deposition are thoroughly examined. New theories describing the kinetics of the co-deposition of composite layers are characterized. The kinetics and mechanisms of electrochemical deposition processes of composite coatings with metallic matrices are discussed. Case studies regarding the electrodeposition of composite coatings based on electrodeposited copper, silver, zinc, tin, nickel, cobalt, and chromium from DES-assisted electroplating baths are described and systematized. The main prospective directions for further research in the discussed scientific area are highlighted.

Keywords: coating; electrodeposition; composite coating; deep eutectic solvent; kinetic; mechanism; properties

1. Introduction

Electrodeposition, as a versatile and extensively utilized method in materials science and surface engineering, holds a central position in tailoring the properties of coatings for diverse applications [1–3]. Within the broad spectrum of electrodeposited coatings, composite coatings have attracted considerable interest because of their unique combination of physicochemical and service properties [4–8].

The fabrication of composite coatings involves the simultaneous electrodeposition of a metallic matrix and dispersed particles of various sizes and chemical compositions from colloidal or suspension plating baths. Once incorporated into the metallic electrodeposited matrix, these dispersed particles enhance different properties, such as corrosion resistance, hardness, and wear resistance, and can introduce novel functional characteristics to the coatings (such as superhydrophobicity; catalytic, electrocatalytic, and photocatalytic activity; self-cleaning capability; etc.). Over recent decades, the emergence of nanostructured materials has been facilitated by electrodeposition techniques, providing avenues for a wide range of nanomaterials, including nanostructured composites [6]. Extensive research efforts have been directed towards creating mechanically strengthened composite layers, improving the magnetic properties of storage devices, decreasing electrical resistance in electronic equipment, and exploring other prospects [4–7].

It is important to highlight that the creation of composite coatings via the electrodeposition technique is limited by the requirement for conductive substrates. Conversely, the electrodeposition method offers several evident benefits, including a relatively uniform dispersion of particles across the coating's thickness, a notably rapid deposition rate, and a low operational temperature (typically below 100 °C), which is markedly lower compared to pyrometallurgical or powder metallurgy approaches. Thus, the electrodeposition method provides a simpler and more accurate means of controlling the microstructure and chemical composition of produced composite films.

Citation: Protsenko, V. Using Deep Eutectic Solvent-Assisted Plating Baths to Electrodeposit Composite Coatings: A Review. *Coatings* 2024, 14, 375. https://doi.org/10.3390/ coatings14040375

Academic Editors: Jose Maria De Teresa, Ricardo Lopez Anton and Sion Federico Olive Méndez

Received: 24 February 2024 Revised: 15 March 2024 Accepted: 21 March 2024 Published: 22 March 2024



Copyright: © 2024 by the author. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). Despite the significant attention given to this field, the current processes of composite electrodeposition remain imperfect, requiring ongoing refinement and further development. Specifically, it should be noted that the majority of publications on this topic have focused on suspension and colloidal deposition baths for the formation of composite layers using aqueous solutions [4–8]. However, aqueous solutions have their limitations; they are prone to rapid aggregation and sedimentation processes, which compromise the stability of the bath composition and impede the electrodeposition of composite coatings. One potential solution to this issue is the adoption of non-aqueous plating baths, specifically with solutions based on the so-called deep eutectic solvents that show particular promise in addressing these challenges.

Deep eutectic solvents, which consist of a hydrogen bond donor and acceptor, have emerged as eco-friendly alternatives to traditional electrolytes due to their minimal toxicity, biodegradability, and broad electrochemical stability range [9–17]. With their distinctive characteristics, deep eutectic solvents offer an exciting opportunity to improve the electrodeposition of composite coatings. One significant advantage of deep eutectic solvents is their dual role as solvents and electrolytes, providing a versatile environment for electrodeposition. The interaction between the components of the DES and the metal ions in the plating electrolyte influences the nucleation, growth, and morphological patterns of the electrodeposited coatings. Understanding these interactions is essential for customizing the properties of composite coatings for specific applications.

A unique characteristic of DESs as solvents is their ability to undergo the extremely flexible control and modification of their composition, defining the tunability of their physicochemical properties [9–11,18]. This feature allows for finely modulating electrodeposition performance, which is important in the production of composite coatings.

Additionally, the environmental impact of electrodeposition processes using DESbased plating baths is a crucial consideration [19,20]. The sustainable and environmentally friendly nature of DESs corresponds well with the increasing demand for green technologies. Reductions in hazardous waste and energy consumption in the electrodeposition process contribute to the vital task of sustainable production.

Up to this point, there have been published reviews dedicated to the electrodeposition of functional coatings using DES-assisted plating baths [14–17,21,22]. However, there is currently a gap in the existing literature regarding a review of publications focusing on the deposition of composite coatings using electrolytes based on DESs. The only exception is [23]. However, this review is somewhat outdated as, since its publication, some new studies have emerged thoroughly and comprehensively examining new aspects of the discussed scientific topic. Taking this into account, this review delves into various aspects of electrochemical deposition using DES-based plating baths, encompassing the impacts of bath composition, deposition parameters, and the resulting microstructure and properties of composite coatings. Additionally, an examination of recent research efforts and advancements in the field provides insights into the current state of understanding and future directions. By elucidating the complexities of electrodeposition utilizing electroplating baths containing deep eutectic solvents, this review aims to contribute to the evolving field of sustainable and efficient electroplating technologies. This review endeavors to navigate through the primary advancements, obstacles, and potential of composite coatings fabricated through the electrodeposition technique using DES-based plating baths.

2. Physicochemical Aspects of DES-Based Systems, Kinetics of Electrochemical Processes, and Their Impact on Composite Electrodeposition

2.1. Colloidal–Chemical Stability of Plating Baths Based on DESs

A specific and inherent characteristic of suspension and colloidal electrolytes used for the electrodeposition of composite coatings is their aggregative and sedimentation instability. In hydrophobic sols and suspensions, particle aggregation (coagulation) of the dispersed phase inevitably occurs due to excess surface energy. As a result, the particles increase in size and then in sediment. All of these are highly undesirable phenomena as they lead to the destruction of the suspension (colloidal) electrolyte, resulting in the instability of the electrodeposition process and deteriorating the functional properties of the formed composite layers. Thus, two main types of stability of colloidal electrolytes are considered: (1) sedimentation stability, which is related to the ability of the dispersed system to resist the sedimentation of particles under the influence of a gravitational field, and (2) aggregative stability, which is the result of the system's ability to resist the aggregation (coagulation) of particles of the dispersed phase. To prevent coagulation and sedimentation, flexible tuning of the electrolyte's chemical composition is typically employed, along with the addition of surfactants and water-soluble polymers and the vigorous stirring of the solutions [6,7].

In their pioneer study [24], Abbott et al. demonstrated a significant advantage of DESs in composite electroplating processes: the stability of particulate suspensions over extended periods, surpassing both aqueous and traditional organic solvent-based baths. This advantage likely stems from a combination of factors, including the higher viscosity of the neat liquid compared to water and the Coulombic screening of surface charge by the ionic liquid, leading to a higher ionic strength. As evident from the data in Table 1, although the density of DESs differs minimally from that of concentrated aqueous electrolytes, their viscosity typically exceeds that of water solutions by 2–4 orders of magnitude (and, in some cases, even more).

Table 1. Viscosity and density of some DESs (based on data from [10]).

Constituents of DES		Salt:Hydrogen		
Salt	Hydrogen Bond Donor	Bond Donor Molar Ratio	Viscosity, cP	(25 °C)
ChCl	urea	1:2	750 (25 °C)	1.25
ChCl	urea	1:2	169 (40 °C)	
ChCl	ethylene glycol	1:2	36 (20 °C)	
ChCl	ethylene glycol	1:2	37 (25 °C)	1.12
ChCl	ethylene glycol	1:3	19 (20 °C)	1.12
ChCl	ethylene glycol	1:4	19 (20 °C)	
ChCl	glucose	1:1	34,400 (50 °C)	
ChCl	glycerol	1:2	376 (20 °C)	1.18
ChCl	glycerol	1:2	259 (25 °C)	
ChCl	glycerol	1:3	450 (20 °C)	1.20
ChCl	glycerol	1:4	503 (20 °C)	
ChCl	1,4-butanediol	1:3	140 (20 °C)	
ChCl	1,4-butanediol	1:4	88 (20 °C)	
ChCl	CF ₃ CONH ₂	1:2	77 (40 °C)	1.342
ChCl	ZnCl ₂	1:2	85,000 (25 °C)	
ChCl	xylitol	1:1	5230 (30 °C)	
ChCl	sorbitol	1:1	12,730 (30 °C)	
ChCl	malonic acid	1:2	1124 (25 °C)	1.25
ZnCl ₂	urea	1:3.5	11,340 (25 °C)	1.63

As stated in [25], the coagulation rate constant, *K*, can be expressed by the following equation:

$$K = \frac{4k_B T}{3\eta W} \tag{1}$$

where k_B is the Boltzmann constant, *T* is the absolute temperature, η is the viscosity of the medium, and *W* is the stability ratio.

If the stability ratio *W* equals unity, *K* precisely coincides with the coagulation rate constant formulated by Smoluchowski for particles that experience no interaction apart from the adhesive force upon contact [26]. Therefore, 1/*W* serves as an indicator of the deviation from the Smoluchowski coagulation rate. *W* is recognized for factoring in the interactions between particles: the interplay resulting from interparticle potentials and

the hydrodynamic interaction that prevents the viscous fluid from interposing between colliding particulates.

Analysis of Equation (1) indicates that the high viscosity of electrolytes based on DESs, which exceeds the viscosity of typical aqueous solutions by several orders of magnitude, should result in extremely low values of the coagulation rate constant. Thus, the high colloidal stability of DES-based solutions compared to water systems is primarily ensured by a kinetic factor, namely, the hydrodynamic resistance of the dispersion medium in the gaps between particles [26]. However, perhaps an equally powerful stabilization factor for colloidal systems in the case of DESs, which are a type of ionic liquid characterized by high ionic strength, is the electrostatic components of disjoining pressure. This component is attributed to the electrostatic repulsion between diffuse parts of electrical double layers. According to the DLVO theory, increased ionic strength should lead to a rise in the disjoining pressure and the height of the maximum on the potential interaction curve. The presence of a noticeable electric charge on the surface of dispersed particles, resulting from the formation of a double electric layer, promotes repulsive interactions and significantly reduces the rate of coagulation. Another stabilizing factor for DES-based colloidal systems is the structural-mechanical barrier, which is realized by the formation of viscous and dense surface layers of the dispersion medium on the particle surfaces, preventing particle agglomeration [26]. Formally, this effect implies a reduction in the value of W in Equation (1). Finally, in a number of cases, the stabilization of colloidal systems with DES dispersion media can be achieved through an adsorption-solvation mechanism: the adsorption of surfactants on particle surfaces and the formation of solvation layers result in a decrease in surface energy, leading to a weakening of the aggregation tendency.

In coarse dispersion systems, instability can manifest as rapid particle sedimentation and subsequent suspension breakdown. The sedimentation rate in a gravitational field is determined by the below equation [26]:

$$v = \frac{2r^2(\rho - \rho_0)g}{9\eta}$$
 (2)

where *r* is the particle radius, ρ is the density of the dispersed phase, ρ_0 is the density of the dispersion medium, *g* is the acceleration of gravity, and η is the viscosity of the dispersion medium.

It is evident that the significantly higher viscosity of suspension solutions based on DESs compared to aqueous electrolytes, according to Equation (2), results in a reduction in the sedimentation rate by several orders of magnitude. As a result, in such suspensions, a highly uniform distribution of particles throughout the volume is maintained for an extended period, which promotes a more stable and productive electrodeposition of composite coatings.

Thus, utilizing DES-based electrolytes enhances the aggregative stability of colloidal systems utilized for electrodeposited composite films. For instance, while Ni–PTFE (polytetrafluoroethylene) composites can be produced from aqueous plating baths only in the presence of certain nonionic or cationic wetting agents, these coatings can be readily obtained in a DES-containing bath without any stabilizing additives as the PTFE particles disperse well in the electrolyte, without requiring wetting agents [27]. Better dispersion of the PTFE particles has been observed in the DES system compared to the water system.

Given their capacity to mitigate nanoparticle agglomeration within the electroplating bath, deep eutectic solvents enable higher nanoparticle loading in the metal matrix compared to aqueous solutions [28]. This effect has been attributed to the diminished hydration force between SiO_2 particles and the non-aqueous electrolyte [29].

The addition of nano- and micro-sized particles to DESs has a significant impact on the colloidal–chemical and rheological characteristics of these fluids. In certain instances, unexpected phenomena have been observed that lack clear and definitive theoretical explanations. For example, when micron-sized particles (such as SiC) were introduced into ionic liquids containing copper salt, a decrease in viscosity was observed in specific concentration ranges [24]. This observation was unexpected, prompting the authors to propose explanations centered around an increase in the fluid's free volume and localized solvent perturbations, where particles functioned as microstirrers within the liquid.

2.2. Kinetics and Mechanisms of Composite Coating Deposition Using DESs

The systematic progress in the electrochemical deposition of composite coatings, including processes utilizing DES-assisted plating baths, requires the development of a suitable kinetic model to understand this complex phenomenon. Various theories have been proposed to elucidate the incorporation of inert particles into growing metal films [6].

For example, Guglielmi [30] proposed a model that describes the integration of particles into a metal matrix as a two-step process of adsorption. In the initial stage, known as "loose adsorption", dispersed particles hosting adsorbed ionic constituents of the electrolyte (primarily ions of the deposited metal) and solvate shells undergo reversible adsorption on the electrode surface, resulting in relatively high surface coverage. According to Guglielmi's model, this stage is primarily of a physical nature. The subsequent stage involves the irreversible "strong adsorption" of dispersed particles, induced by the reduction in metal ions adsorbed on the particle surface. Subsequently, the particles become trapped by the growing metal matrix. This second adsorption stage is believed to have an electrochemical nature. Guglielmi suggested that the loose adsorption of dispersed particles in the first stage is reversible and, therefore, the degree of surface coverage due to loose adsorption can be described using the classical Langmuir adsorption isotherm.

Although Guglielmi's kinetic model of coating co-deposition has gained acceptance and validation from researchers [6,7], it is crucial to acknowledge that this theory is not flawless and has several shortcomings. One of the key drawbacks of this theory is that a physical model integrating both the reversible and the irreversible adsorption of particles of the same nature on the same surface seems inherently contradictory and overly complex and lacks strong substantiation. The assumption of the a priori reversible nature of the adsorption of dispersed particles in the initial stage of the process is made without accompanying evidence.

Despite numerous efforts to develop improved kinetic models for the electrodeposition of composite coatings [31–39], most current models still have shortcomings [7]. It is worth noting that nearly all previously proposed theories in this area either explicitly or implicitly assume that the adsorption of dispersed particles on a growing metal surface is reversible. However, it is well established that the adsorption of dispersed particles on solid surfaces tends to be irreversible [40–42], a critical aspect often neglected in many theoretical models aimed at describing the kinetics of the electrodeposition of composite coatings.

To address this concern, ref. [43] introduced a novel kinetic model for the electrodeposition of composite coatings based on the assumption of the irreversible adsorption of dispersed particles onto the electrode surface. This theoretical concept suggests that the amount of dispersed phase incorporated into the electrodeposited composite coating is determined by the kinetics of the irreversible adsorption stage. The key difference between the kinetic model developed in [43] and Guglielmi's theory is illustrated in Figure 1. Guglielmi's model suggests that the adsorption/desorption processes of dispersed particles occur rapidly, reaching equilibrium surface coverage primarily through loose adsorption (Figure 1a). However, only a small fraction of these adsorbed particles are subsequently integrated into the composite coatings via strong adsorption. In contrast, the proposed model suggests that the steady-state surface concentration of dispersed particles is controlled by the rate of two processes: the fixation of particles on the surface through incorporation into the deposit as they become part of the metal matrix (Figure 1b).

In [43], the following equation was proposed to describe the co-deposition process of composite coatings and determine certain process parameters:

$$\frac{1}{\alpha} = \frac{6q_{Me}i}{kC_0\pi\rho_{Me}d^3} + \frac{1}{\alpha_{\max}}$$
(3)

where α is the degree of surface coverage with adsorbed particles, α_{max} is the maximum degree of surface coverage, *k* is the adsorption rate constant, *C*₀ is the concentration of dispersed particles in the electrolyte volume, *i* is the partial current density of metal deposition, q_{Me} is the electrochemical equivalent of the metal, ρ_{Me} is the density of the metal, and *d* is the diameter of particles.



Figure 1. Schematic representations illustrating the incorporation of dispersed phase particles into the composite coating based on models assuming reversible (**a**) and irreversible (**b**) adsorption of particles on a metal surface. It should be noted that the length of the arrows in (**a**) does not accurately represent the scale of the corresponding fluxes as the rate of reversible adsorption/desorption can be orders of magnitude higher than the rate of particle inclusion in the composite coating. Reprinted from [43], copyright 2022, with permission from Elsevier.

According to Equation (3), a graph plotted in coordinates $\frac{1}{\alpha} vs. \frac{1}{C_0}$ should result in a straight line with an intercept at $\frac{1}{\alpha_{max}}$, facilitating the determination of the value of α_{max} . The slope of this resultant straight line equals $\frac{6q_{Mel}}{k\pi\rho_{Mel}d^3}$, enabling the calculation of the adsorption rate constant *k*. The suggested model in [43] was employed to interpret experimental data concerning the kinetics of the electrochemical deposition of nickel–titania composite coatings deposited using both an aqueous electrolyte and an electrolyte prepared based on a deep eutectic solvent. Plots depicted with coordinates $\frac{1}{\alpha} vs. \frac{1}{C_0}$ for Ni–TiO₂ composite coatings fabricated from an electrolyte based on a DES exhibited a linear trend (Figure 2). Deviations from linearity were observable for the smallest values of $\frac{1}{C_0}$, corresponding to high degrees of surface coverage near the maximum, where the condition $(1 - \alpha) \approx 1$, as assumed during the derivation of Equation (3), was no longer satisfied. The values of *k* and α_{max} were found for various deposition current densities using Equation (3) for the linear segments of dependences in Figure 2 (Table 2).

Table 2. Calculated kinetic parameters regarding electrodeposition of Ni–TiO₂ composite coating from an electrolyte based on DES. Reprinted from [43], copyright 2022, with permission from Elsevier.

	Parameter *		
Current Density (A dm ⁻²)	<i>k</i> (m s ⁻¹)	α _{max}	R^2
1	2.612×10^{-6}	0.256	0.997
1.5	2.159×10^{-6}	0.220	0.999
2	1.554×10^{-6}	0.158	0.999
3	1.520×10^{-6}	0.093	0.998

* Note: R² stands for the calculated coefficients of determination.





While the adsorption rate constants for the incorporation of titania particles into the nickel matrix deposited remained relatively consistent for both the aqueous electrolyte and the DES-based electrolyte (approximately 10^{-6} m s^{-1}), the value of *k* was notably higher for the DES-based electrolyte under similar conditions [43]. For instance, at a current density of 2 A dm⁻², the adsorption rate constants were $0.453 \times 10^{-6} \text{ m s}^{-1}$ and $1.554 \times 10^{-6} \text{ m s}^{-1}$ for coatings deposited using an aqueous solution and a deep eutectic solvent, respectively. This disparity was attributed to the different sizes of titania particles used. Nanoscale particles, such as Degussa P 25, exhibit higher surface energy compared to submicron-sized particles. Under specific circumstances, this heightened surface energy may contribute to the formation of a stronger adhesive bond with the surface of the deposited matrix, resulting in an increased adsorption rate constant. This phenomenon is likely linked to the observation that composites obtained from the DES-based electrolyte incorporate a significantly larger amount of the TiO₂ phase compared to coatings from an aqueous electrolyte (at comparable mass concentrations of the dispersed phase in the electrolytes under consideration), and they exhibit higher values of α_{max} .

The relationship between the adsorption rate constant and current density revealed a significant distinction between the two electrolyte types under consideration [43]. For the aqueous electrolyte, an elevation in current density (essentially, an increase in cathode polarization) corresponded to a rise in the value of *k*. Conversely, for the DES-based electrolyte, an increase in current density led to a decrease in *k*. This observed effect was presumed to stem from notable differences in the structure of the electric double layer in aqueous and DES-based electrolytes [44,45].

Mamme et al. [45] showed that in DES-based systems, the double layer exhibits a sophisticated cluster structure comprising multiple adsorption layers, each enriched with specific molecular or ionic components from the solution. The structure and composition of these layers are notably influenced by the electric charge of the electrode. On a negatively charged electrode surface, two layers form, enriched with hydrogen bond donor molecules arranged differently in relation to the electrode surface. It was postulated [43] that the emergence of multiple layers containing ionic and molecular components within the double layer (essentially, its structural complexity) with an increase in the cathode polarization hampers the complete or partial disruption of adsorption layers and solvate shells. This hindrance serves as a prerequisite for the irreversible adsorption of dispersed particles onto the surface of the growing nickel layer and the formation of a strong adhesive bond. Ultimately, this phenomenon resulted in the observed reduction in the adsorption rate constant with an increase in cathode current density (Table 2).

A comparison of data regarding the incorporation of titania nanoparticles into the nickel electrodeposited matrix in aqueous solutions and DES-based plating baths revealed [46] that the DES-assisted system offers a relatively lower TiO₂ content compared to water solutions under otherwise similar conditions. In particular, it was noted that the maximum TiO₂ content reaches 2.35 wt.% and 11.58 wt.% when using DES-assisted electrolytes (without the addition of water) and aqueous electrolytes, respectively. This observation was elucidated through the following rationale. Each particle suspended in a plating bath is enveloped by a thin layer of the electrolyte, which must be removed to be integrated into the growing metal electrodeposit. Likewise, a thin layer of electrolyte components should be removed from the electrode surface during the entrapment of particles into the depositing matrix. This process also encompasses the potential presence of adsorbed layers on the electrode that necessitate partial or complete disruption. It is imperative to consider that DES-containing electrolytes diverge from aqueous counterparts due to significantly higher viscosity and density. Consequently, DES-based systems necessitate substantially more time and energy to destroy dense and viscous films formed on the surfaces of both particles and a growing metal matrix, impeding the rate of particle inclusion into deposits and thereby diminishing the maximum available content of an inert dispersed phase in the deposited composite layer.

At the same time, the physicochemical properties of DESs can be finely tuned by the addition of water, which, in this case, serves not only as a solvent but also as an additional special hydrogen bond donor [47]. It has been demonstrated [48] that the addition of water to a colloidal electrolyte results in a significant decrease in viscosity, facilitating the easier disruption of surface layers. Furthermore, the reduction in electrolyte viscosity accelerates the transfer of colloidal particles to the electrode surface. These phenomena account for the observed increase in TiO₂ content when water is introduced into the electrolyte. However, once a certain threshold value is reached, the TiO₂ content in the composite coating remains constant regardless of the water content [48]. It is understood that a certain "burial time" is necessary for a colloidal particle adsorbed on the surface to become entrapped in a growing metal matrix [36]. An adsorbed particle can only be integrated into a composite if its "residence time" exceeds the "burial time". It seems that the residence time begins to decrease at a certain level of added water due to the accelerated desorption of particles caused by the competitive adsorption of water molecules on the surface of hydrophilic nickel. Consequently, the TiO₂ content in composite coating stops increasing.

It has been demonstrated [24] that the co-deposition of electrochemically inert particles of the dispersed phase affects the kinetics of electrochemical deposition of the metal matrix. Specifically, the cyclic voltammograms registered during the electrodeposition of copper from DES-assisted plating baths with 10 wt.% Al₂O₃ or SiC (Figure 3) indicate a significant decrease in current upon the addition of particulates to the solution. Analysis of the data led to the conclusion that the observed reduction in the current can be explained by the physical blocking of the electrode surface by the non-conductive particulate matter, thereby effectively diminishing the conductive area of the electrode surface. Additionally, Figure 3 illustrates some variation in peak potentials corresponding to the different types of deposits, particularly noticeable in the anodic stripping response. This variability is expected as the peak position is influenced by the timescale; therefore, the copper components in different composites will be electrochemically dissolved at a rate that is sensible for the composite composition.

In [24], the consistent kinetic stability of solutions based on a DES throughout the experimental period was underscored, indicating the absence of the settling of Al_2O_3 particles. This implies that the sedimentation of alumina particles did not significantly affect their overall incorporation rate. It was presumed that the principal mechanism governing the inclusion of particles into the deposited metal matrix was the irreversible adsorption mechanism discussed earlier. Moreover, it was noted that larger particles were more effectively incorporated at lower solution concentrations, while both particle sizes exhibited preferential distribution into the metal deposit at higher concentrations.



Figure 3. Voltammograms registered on platinum working electrode in electrolyte containing $0.02 \text{ mol dm}^{-3} \text{ CuCl}_2 \cdot 2\text{H}_2\text{O}$ dissolved in deep eutectic solvent (eutectic mixture of ethylene glycol and choline chloride with the addition of either 10 wt.% Al₂O₃ or SiC. Potential sweep was 0.010 V s^{-1} ; silver wire was used as quasi-reference electrode. Reprinted from [24], copyright 2009, with permission from Royal Society of Chemistry.

The addition of SiO₂ nanoparticles into a DES-based solution containing dissolved Ni(II) salt was observed to alter the response of cyclic voltammetry [28]. Specifically, the peak potential of Ni(II) ion electroreduction shifted towards more positive values, accompanied by an increase in maximum current density upon the introduction of SiO₂ nanoparticles into the DES. The authors proposed two potential roles of SiO₂ particles in the electrodeposition process. Firstly, active SiO₂ particles may serve as efficient preferential nucleation sites, thereby facilitating the electrochemical deposition process. Secondly, SiO₂ nanoparticles could directly take part in the electrode reaction and catalyze the electrodeposition of nickel.

The nucleation and growth processes of Ni–SiO₂ composite deposition were investigated through the chronoamperometry technique [29]. It was observed that the nucleation of pure nickel closely followed a three-dimensional progressive nucleation mechanism at more positive potentials, gradually transitioning to a three-dimensional instantaneous nucleation mechanism as the applied potential shifted towards more negative values. However, in the Ni–SiO₂ system, nucleation predominantly followed a three-dimensional instantaneous mechanism. As the concentration of SiO₂ increased, the nucleation mode gradually deviated from the theoretical model. This difference in nucleation behavior between the deposition of pure nickel and Ni–SiO₂ composites was attributed to changes in the surface charge of particles and the thickness of the electrical double layer resulting from the presence of SiO₂ nanoparticles. The observed deviations in nucleation behavior in the Ni–SiO₂ system were associated with the growth process, which exhibited diffusion and partial kinetic rate control. The partial kinetic control of growth may be attributed to the chemical interaction between Ni(II) ions and the unsaturated bonds of oxygen atoms on the surface of silica particles.

A comprehensive investigation into the nucleation and growth mechanism of the electrochemical deposition of Ni–SiC composites in an ethylene glycol/choline chloride-based DES containing either micro- or nano-sized SiC particles was conducted by Li et al. [49]. In the absence of added SiC particles, the nucleation of nickel typically followed the three-dimensional progressive mechanism, particularly at relatively positive applied potentials. However, as the potential shifted negatively, the nucleation mode gradually transitioned towards a three-dimensional instantaneous mechanism (Figure 4). These observations are consistent with the findings reported in [29]. However, upon introducing micro-sized SiC particles (0.3 μ m) into the DES plating electrolyte, the nucleation mechanism of nickel

initially aligned with three-dimensional instantaneous nucleation and then showed some deviation from the theoretical pattern. Conversely, the nucleation of nickel in the presence of nano-sized SiC particles (40 nm) closely adhered to the three-dimensional instantaneous nucleation mechanism. Thus, it can be inferred that micro- and nano-sized particles exert distinct effects on the nucleation and growth mechanism of the metal [49].



Figure 4. Current vs. time curves plotted in dimensionless coordinates for deposition of nickel and Ni–SiC composites: (**a**) without SiC particles, (**b**) with micro-SiC particles, and (**c**) with nano-SiC particles. Reprinted from [49], copyright 2015, with permission from Royal Society of Chemistry.

As evident from numerous case studies discussed below, the use of electrolytes based on DESs often yields coatings with a nanocrystalline structure [23]. This may be explained by the effect of several key factors. Firstly, DES-based solutions typically exhibit higher viscosity and density compared to aqueous electrolytes. This difference in fluid properties can slow down diffusion processes and crystal growth rates, favoring the formation of nanocrystalline structures. Secondly, DESs may have distinct effects on the kinetics of crystal growth compared to aqueous solutions due to their unique chemical properties and reactivity. Thirdly, the chemical interaction between the electrode surface and DES-based electrolytes may differ from that in aqueous solutions, influencing nucleation and crystal growth processes. Aqueous electrolytes without the addition of surfactants typically lead to the formation of microcrystalline structures due to rapid nucleation and growth processes facilitated by the high mobility of ions in the solution and rapid diffusion. However, the use of DESs can modify these conditions, slowing down surface diffusion and charge transfer and promoting the formation of nanocrystalline structures. In summary, the utilization of DES-based plating electrolytes alters the deposition conditions, leading to the formation of nanocrystalline coatings, whereas, under similar conditions, microcrystalline coatings are typically obtained from aqueous electrolytes.

3. Case Studies

Below, we will delve into case studies described in the literature concerning the electrodeposition of composite coatings using DES-based electrolytes, along with the characterization of the properties and potential applications of the resulting composite layers. The analysis will be structured according to a classification based on the chemical nature of the material constituting the deposited metal matrix, which is commonly used when discussing data concerning the electrochemical synthesis of composite layers.

3.1. Copper-Based Composites

The study conducted by Abbott et al. [24] marked a pioneering investigation into the electrodeposition of composites using DESs based on choline chloride. The researchers explored the electrodeposition process of $Cu-Al_2O_3$ and Cu-SiC composites utilizing two distinct ionic liquids: one comprising a eutectic mixture of choline chloride and ethylene glycol (commercially known as ethaline) and the other comprising a eutectic mixture of choline chloride and ethylene adumnia (with particle sizes of $0.05 \ \mu m$ and $1.0 \ \mu m$) or silicon carbide (ranging from 1 to $3 \ \mu m$) were added to the electroplating baths. The loading of Al_2O_3 and SiC particles within the resulting electroplated films was found to be significantly influenced by the particulate concentration in the solution while remaining largely unaffected by the concentration of copper metal ions or the duration of the process. An elevation in the concentration of colloidal particles in the solution corresponded to an increase in their content within the composite electrodeposits.

An important observation from Abbott et al. [24] is that at lower solution concentrations, larger particles exhibited a more efficient incorporation compared to smaller ones. However, at higher concentrations, both particle sizes were preferentially partitioned into the metal deposit. The primary mechanism attributed to the inclusion of particles was identified as diffusion/convection driven by the concentration gradient.

The process of the electrodeposition of Cu/nano-SiC composites from DESs based on ethylene glycol and the influence of the addition of two surfactants, sodium dodecyl sulfate and cetyl trimethyl ammonium bromide, were investigated [50]. It was observed that sodium dodecyl sulfate reduced the SiC content, while cetyl trimethyl ammonium bromide increased the loading of inert particles in the coatings. The presence of surfactants also affected the surface morphology of the composite coatings.

3.2. Silver-Based Composites

Abbott et al. [51] investigated the electrodeposition of a silver-based composite utilizing deep eutectic solvents comprising ethylene glycol and choline chloride for the first time. The plating electrolyte contained 0.1 mol dm⁻³ silver chloride dissolved in ethaline. The addition of nano-sized SiC particles (50 nm) did not alter the surface morphology of the silver matrix; however, it led to a doubling of the microhardness of the electrodeposited coatings. Interestingly, increasing the size of the SiC particles from 50 nm to 2 mm did not affect the microhardness of the composites, although it did result in a significant decrease in wear volume (from 4440 μ m³ to 4263 μ m³, respectively). This finding is noteworthy as it suggests the feasibility of depositing silver composites with enhanced wear resistance for electrical contacts using DES-assisted plating electrolytes. The inclusion of Al₂O₃ nanoparticles (50 nm) had the most pronounced effect on the microhardness of the deposits; however, the wear volume and surface morphology were comparable to those of coatings containing SiC particles of the same size. Therefore, it can be concluded that the friction coefficient and wear resistance are determined by the nature rather than the size of the added particles [51].

3.3. Zinc-Based Composites

Marín-Sánchez et al. [52] reported the cathodic electrodeposition of Zn–cerium oxides using the deep eutectic solvent choline chloride-urea (reline). Zinc and cerium chloride salts (ZnCl₂ and CeCl₃·7H₂O) were added to the plating electrolyte both separately (0.3 mol dm⁻³ in each case) and jointly (at the Zn:Ce ratio of 3:1). Cerium was integrated into the electrodeposit as a mixed oxide Ce₂O₃ + CeO₂ within the zinc metal matrix. The surface morphology and chemical composition of the coatings varied with the current density of the electrodeposition process. The maximum cerium content, averaging 8.30 ± 1.36 at.%, was attained at current densities ranging from 1.13 to 0.75 A dm⁻², with cerium predominantly existing in the form of mixed oxides: 50.6% Ce₂O₃ + 49.4% CeO₂. Electrochemical corrosion tests demonstrated similar corrosion rates for all coatings. In the case of defects in the zinc–cerium oxide coating, active migration of cerium was observed, potentially augmenting the protective properties of the coating in comparison to "pure" zinc.

Li et al. [53] investigated the electrochemical deposition of zinc–graphene oxide (zinc–GO) composite coatings using a plating bath containing a eutectic mixture of urea and choline chloride. The concentration of ZnCl₂ in the plating solution was 0.2 mol dm⁻³, while the concentration of GO was 0.05 g L⁻¹ or 0.10 g L⁻¹. It was observed that the graphene oxide sheets exhibited extremely good dispersion stability with this DES. GO particles, when incorporated into the growing zinc metallic matrix, served as favorable nucleation sites, thereby accelerating the electrodeposition reaction. The presence of graphene oxide significantly impacted the surface morphology and phase structure of the deposited layers. Consequently, GO particulates could effectively enhance nucleation rates, reduce the growth rates of zinc nuclei, alter the grain shape from polyhedron to granule, and refine the grain structure (Figure 5). The zinc–GO composite films demonstrated superior corrosion stability compared to pure zinc, with corrosion resistance further improving as the GO content grew.



Figure 5. SEM micrographs depicting the surface morphology of zinc-based coatings: (a) without graphene oxide particles in the plating solution, (b) with 0.05 g L^{-1} graphene oxide, and (c) with 0.10 g L^{-1} graphene oxide. Reprinted from [53], copyright 2015, with permission from Royal Society of Chemistry.

3.4. Tin-Based Composites

The electrodeposition of composite coatings comprising a tin matrix with embedded reduced graphene oxide (rGO) was investigated, utilizing a deep eutectic solvent as the plating solution [54]. The electrodeposition was carried out from an ethaline-based solution, containing 0.7 M SnCl₂·2H₂O with and without 20 mg L^{-1} rGO, at a temperature of 70 °C under constant magnetic stirring. It was demonstrated that this electrolytic medium facilitated the creation of a stable and uniformly dispersed graphene oxide solution, enabling the subsequent integration of rGO sheets into the Sn matrix. The deposition process of Sn-rGO composites involved nucleation and three-dimensional growth controlled by diffusion, with nucleation transitioning from progressive to instantaneous as the overpotential increased. Uniform Sn-rGO composite films were successfully electrodeposited, demonstrating good adhesion to the copper substrate. X-ray diffraction analysis revealed that the presence of rGO in the coatings reduced the preferred orientation of tin growth along the planes (101), (211), (301), and (112). The average crystallite sizes ranged from 82 to 98 nm for pure tin and from 77 to 92 nm for Sn-rGO deposits. An enhancement in corrosion resistance was observed for the Sn-rGO composite films compared to pure tin. Furthermore, the results indicated satisfactory solderability of the coatings, indicating that

the electrochemically deposited Sn-rGO composite could serve as an efficient solder layer, as evidenced by wetting angles of about 44°.

3.5. Nickel-Based Composites

The majority of the published literature on composite electrodeposition using DESbased plating solutions focuses on materials with a nickel matrix. For example, Li et al. [28] proposed a method for the in situ synthesis of SiO₂ nanoparticles in a DES-assisted medium (ethaline), enabling the synthesis of highly dispersed SiO₂ nanoparticles and the electroplating of a homogeneous nickel matrix with evenly distributed silica nanoparticles. In this process, tetraethyl orthosilicate (Si(OC₂H₅)₄) was blended with ethaline and hydrolyzed with the addition of a 10 wt.% hydrochloric acid solution. The resulting silica particles had diameters ranging from 40 to 65 nm. The amount of captured silica nanoparticles in the composite films reached 5.13 wt.%. Friction and wear tests revealed that the uniform dispersion of silica nanoparticles in the Ni matrix notably enhanced the tribological performance of the composite electrodeposited layers, leading to improved wear strength and stable coefficients of friction.

In [29], SiO₂ nanoparticles were co-deposited into a nickel matrix using an ethalinebased DES through pulsed electrolysis. The concentration of NiCl₂·6H₂O in the electrolyte was 0.2 mol dm⁻³, while the contents of nano-sized SiO₂ (15–30 nm) were 0, 5, 15, 25, 35, and 45 g/L. It was suggested that the presence of these embedded silica nanoparticles significantly influenced the nucleation and growth processes, microstructure, and chemical composition of the composite electrodeposits. The maximum content of embedded SiO₂ particles (approximately 4.69 wt.%) was detected in the absence of any stabilizing additives. In comparison to pure nickel coatings, the Ni–SiO₂ nanostructured composite coatings demonstrated notably improved corrosion resistance, with the level of enhancement correlating to the increase in the SiO₂ particulate loading in the electrodeposited films (Figure 6, Table 3) [29].



Figure 6. Open circuit potential (OCP) vs. time plot (**a**) and potentiodynamic polarization curves (**b**) of nickel and nickel–SiO₂ composite coatings recorded in 3.5% solution of NaCl. Reprinted from [29], copyright 2016, with permission from Elsevier.

Table 3. Parameters derived from corrosion test of nickel and nickel–SiO₂ composite coatings in 3.5% solution of NaCl. Reprinted from [29], copyright 2016, with permission from Elsevier.

Specimens	E _{corr} (V vs. Ag/AgCl)	<i>i</i> _{corr} (A/cm ²)
Pure Ni	-0.72	$3.92 imes 10^{-5}$
Ni-5g/LSiO ₂	-0.57	3.23×10^{-6}
Ni-25g/LSiO ₂	-0.43	$2.89 imes10^{-7}$

Ni–SiC composite coatings were produced through a pulsed electrodeposition technique using an ethaline-based DES [49]. Silicon carbide particles of varying sizes (0.3 µm or 40 nm) were employed in formulating the plating solutions, the contents of the microor nano-sized SiC particles being 5, 10, 15, 20, 25, and 30 g L⁻¹. The electrolyte contained also 0.2 mol dm⁻³ NiCl₂·6H₂O. Both nano- and micro-scale SiC particles were uniformly dispersed within the electrodeposited Ni matrix. The influences of particle concentration in the electrolyte, current density, and solution stirring rate on the silicon carbide particle content in the composite electrodeposits were investigated. The maximum loadings of nano- and micro-sized SiC dispersed phases in the composite layers were found to be up to 5.37 wt.% and 12.80 wt.%, respectively. The obtained composite films exhibited greater hardness and enhanced wear resistance compared to pure Ni coatings. Specifically, while the microhardness of pure nickel was approximately 289 HV, it increased to 895 HV and 716 HV with the introduction of nano- and micro-sized SiC particulates into the coatings, respectively [49].

Ni–PTFE composite coatings deposited via the electrodeposition method have garnered significant interest owing to their favorable properties such as low friction coefficient, solid lubrication, and excellent water repellency. Research by You et al. [27] introduced a deep eutectic solvent-based bath for electrodepositing Ni–PTFE composite layers, eliminating the need for wetting agents. Thus, the electrolyte contained 1.0 mol dm⁻³ NiCl₂·6H₂O in ethaline and the concentration of PTFE particles was 5 or 10 g L⁻¹. The obtained coatings contained approximately 3 wt.% of PTFE. The incorporation of PTFE contributed to the improved wear resistance of the composites compared to pure nickel coatings. However, contrary to expectations, potentiodynamic polarization investigations revealed that pure nickel exhibited superior anticorrosion behavior compared to the Ni–PTFE composite coatings: an increase in the PTFE content in the investigated composite films resulted in a more negative corrosion potential and higher corrosion current [27].

A series of scientific publications [43,46,48,55–57] investigated the electrochemical deposition behavior of Ni–TiO₂ composite coatings using plating baths formulated with deep eutectic solvents. Furthermore, various properties of the resulting coatings were characterized. Nickel–TiO₂ composite coatings, deposited from DES-based electrolytes without any specific additives, contained titania particles in concentrations not exceeding 2.35 wt.% [46]. As indicated by the data presented in Figure 7, an increase in the water content in the plating electrolyte notably elevated the concentration of the titania particles in the composite films (up to ≈ 10 wt.%) [55].



Figure 7. Influence of water concentration in the electrolyte on the TiO₂ content in electrodeposited composite layers. Current density was 1 A dm⁻². Titanium dioxide particle concentration in the electrolyte was 5 g L⁻¹. The content of Ni(II) ions in ethaline was 1 mol dm⁻³. Reproduced from [55], copyright 2022.

Electrodeposition using electrolytes based on DESs resulted in the formation of nanocrystalline films, with crystalline sizes ranging from approximately 6 to 10 nm, contrasting with the "typical" microcrystalline nickel obtained from aqueous nickel plating

baths [55]. This observation corroborates earlier findings [58–60], underscoring the ability to produce nanostructured nickel coatings using DES-assisted electroplating baths. Notably, the electrodeposition of nickel matrices in deep eutectic solvents proceeds under conditions of strong adsorption of both organic and inorganic components of the plating solution on the Ni surface. This phenomenon impedes surface diffusion, slows down crystallite growth rates, and ultimately facilitates the deposition of nanostructured coatings. Moreover, not only do organic components of DESs contribute to this effect but dispersed TiO₂ nanoparticles can also act as specific surfactants impeding the rate of Ni electrodeposition [55].

It was revealed that the incorporation of TiO_2 nanoparticles into a nickel matrix, along with an augmentation in their concentration within the electrodeposits, induces a shift in corrosion potential towards more positive values, an enhancement in polarization resistance, and a reduction in corrosion current density [56]. The improvement in the corrosion resistance of the coatings was attributed to the barrier effect exerted by the dispersed phase particulates and the creation of corrosion microcells, which promoted the deceleration of localized corrosion.

The electrocatalytic activity of nickel coatings and electrodeposited Ni/TiO₂ composites in a hydrogen evolution reaction (HER) was assessed using linear voltammetry in an alkali water electrolyte (Figure 8) [48]. Remarkably, the nickel coating fabricated with the DES-based electrolyte exhibited markedly improved electrocatalytic performance in the HER compared to the one produced from an aqueous electrolyte. This improvement was clearly observed in the polarization curve, which shifted towards more positive electrode potentials. Furthermore, the introduction of titania particles into the Ni matrix led to a shift in the polarization curve towards more positive electrode potentials, indicating an additional enhancement in electrocatalytic activity.

The findings presented in [46,48,55] suggest that the fabrication of nanostructured Ni/TiO₂ composite coatings using DESs holds promise for the advancement of efficient electrocatalysts in the synthesis of "green" hydrogen [61,62]. It is noteworthy that electrodeposited Ni/TiO₂ composite layers demonstrate not only electrocatalytic capabilities but also exhibit photocatalytic activity in the photochemical degradation of methylene blue organic dye in aqueous solutions [46]. This observation could pave the way for the development of novel heterogeneous photocatalysis processes (TiO₂/UV) for wastewater treatment, leveraging electrodeposited metal matrices as reliable supports for titania particles [63,64].

Liu et al. [65] reported their investigation into the influence of boric acid and water on the deposition process of Ni–TiO₂ composite coatings using a deep eutectic solvent. Their findings revealed that the addition of boric acid to the plaiting bath yields an acidic medium, preventing the formation of hydroxide nickel(II) compounds and the decomposition of the DES constituents. Therefore, boric acid seems to be an important additive in the deposition process, particularly when employing a deep eutectic solvent-based nickel plating solution. Nevertheless, once the boric acid concentration in the composite electrolyte surpasses approximately 9 g L^{-1} , the internal stress within the coating escalates, leading to the emergence of minor cracks in the coating structure. In addition, the introduction of extra water into the plating bath is advantageous in reducing the viscosity of the deep eutectic solvent and augmenting its conductivity. Consequently, this leads to a significant increase in the current density of nickel (II) ion electroreduction. Furthermore, water plays a crucial role in altering the complexation state of Ni(II) ions, resulting in the formation of a coating characterized by smaller crystallite dimensions. However, it is essential to note that an excessive amount of added water can facilitate the deposition of large agglomerated TiO₂ particles within the coating, posing potential challenges.

Several studies [66–68] have reported the electrochemical deposition of composite films that incorporate various forms of nanostructured carbon into a nickel matrix. For example, uniform nickel–multiwalled carbon nanotube (Ni–MWCNT) composite layers were fabricated using reline-based plating baths [66]. The electrolytes exhibited a remarkably stable dispersion of both initial and oxidized MWCNTs, leading to a homogeneous

distribution of MWCNTs within the deposited nickel matrix. It was observed that the crystallinity, surface morphology, roughness, and corrosion resistance of the resulting composites were directly affected by the presence of MWCNTs.



Figure 8. Voltammetry responses characterizing hydrogen evolution reaction on Ni (1, 2) and Ni– TiO₂ (3) coatings in 1 M NaOH solution at 298 K. Electrodeposition was performed using aqueous electrolytes (1) and DES-assisted plating baths (2, 3). Current density was 10 mA cm⁻². The concentration of titania in the DES-based electrolytes was 5 g l⁻¹. The DES-based baths contained (**A**) no extra water, and (**B**) 6 mol L⁻¹ extra water. The content of NiCl₂·6H₂O was 1 mol L⁻¹. Reprinted from [48], copyright 2019, with permission from Elsevier.

Liu et al. [67] investigated the electrodeposition of composites with a Ni matrix using reline DES with the addition of dispersed carbon nanotubes (CNTs). The electrolyte contained 50 g L^{-1} NiCl₂·6H₂O and 0.5 mol L^{-1} CNT. The electroplated composites were found to have larger crystalline grain sizes of nickel compared to the pure deposited Ni. Moreover, the incorporation of CNTs led to an increase in surface roughness, rising from 58 nm to 94 nm following the introduction of CNTs into the coatings. The Ni–CNTs composites exhibited an exceptionally low friction coefficient and demonstrated improved tribological behavior [67]. Xiang et al. [68] addressed the challenge of graphene agglomeration in DES-assisted plating baths to synthesize graphene-reinforced composite coatings via the electrodeposition technique. The electrolyte had the following composition: 37.4 wt.% CH₃CONH₂ (acetamide), 28 wt.% CO(NH₂)₂ (urea), 34.6 wt.% NH₄NO₃, 0.05 mol L⁻¹ NiCl₂·6H₂O, and 30 g L⁻¹ H₃BO₃. The exfoliated graphene derived from the graphite anode was a source of the dispersed phase in the plating bath. The graphene content in the prepared coatings reached approximately 23.9 wt.%. The introduction of graphene did not alter the orientation of the nickel crystal faces; however, it led to a significant refinement in the grain size. The resulting composite coating exhibited exceptional microhardness compared to the pure Ni coating (Figure 9). Additionally, the composite coating demonstrated

reliable lubricating properties, with a relatively low friction coefficient (approximately 0.14) and a significantly reduced wear rate, decreased by over 60% and tenfold, respectively, in comparison to the nickel film (Figure 10).



Figure 9. Comparison of microhardness of nickel coating and nickel–graphene composite coating. Reprinted from [68], copyright 2019, with permission from Elsevier.



Figure 10. Comparison of wear rate and friction coefficient of nickel coating and nickel–graphene composite coating. Reprinted from [68], copyright 2019, with permission from Elsevier.

Wang et al. [69] investigated the electrochemical deposition of composite layers of Ni-activated carbon and Ni-nano-carbon (50 nm) in a plating electrolyte based on ethaline. The used electrolytes had the following compositions: 0.2 M NiCl₂·6H₂O and 0, 2, 4, 6, 8, 10, 12, or 14 g L^{-1} activated carbon or 50 nm carbon particles without any pre-treatment. It was demonstrated that the electrodeposited composite coatings had a three-dimensional, flower-like microstructure. SEM images of the surface of the nickelnano-carbon coatings (Figure 11) revealed that the carbon nanoparticles embedded within the metal matrix yielded a flower-like microstructure, reminiscent of chrysanthemums. Enhanced electrocatalytic activity towards hydrogen evolution was observed when using the electrodeposited composite as electrocatalysts. It should be noted that the variety of patterns of surface morphologies detected in [69] and illustrated in Figure 11 indicates that the electrodeposition of composite layers from electrolytes based on DESs reveals additional possibilities for controlled influence on the growth mechanism, particularly the ability to flexibly change between growth mechanisms such as "layer-by-layer", "layer-plus-island", and "island" growth. In traditional aqueous electrolytes, this switch between mechanisms can be achieved by varying the parameters of pulsed electrolysis [70].

A study by Cherigui et al. [71] reported the electrochemical deposition of nickel-based nanostructures onto a glassy carbon electrode using reline. It was demonstrated that the electrocatalytic hydrolysis of residual water present in the deep eutectic solvent occurred at a relatively negative electrode potential, leading to the formation of a hybrid Ni + Ni(OH)₂

adsorbed film. Such coatings can be viewed as composite; yet, the hydroxide particles were not directly introduced into the plating bath as a dispersed phase but rather formed in situ on the electrode surface. These electrodeposited composite layers hold significant promise for generating supported nanostructures in a controlled and efficient manner, offering potential benefits across a wide spectrum of applications.

Microflakes composed of mixed cerium molybdenum oxide hydrates were synthesized from soluble precursors and co-deposited with a nickel matrix to form Ni–Ce,Mo oxide composite coatings [72]. It was concluded that DES-assisted electroplating solutions made it possible to successfully prepare composite layers, resulting in nanocrystalline Ni matrices with a smaller crystallite size compared to the pure nickel electrodeposits (6.3 nm and 10.4 nm, respectively). The corrosion behavior of these composite coatings in an aggressive 0.05 M NaCl solution was extensively investigated. During corrosion, NiO changed into Ni(OH)₂, whereas oxides of molybdenum were removed from the coating surface. These findings hold potential interest in creating novel surface films exhibiting self-healing behavior.

An interesting approach to the electrodeposition of composite coatings involves the co-deposition of a metallic matrix with metallic particles of a dispersed phase. For instance, the patterns of electrodeposition and the properties of the resulting composites from electrolytes based on DESs containing dissolved nickel (II) salt and nanoparticles of titanium or aluminum have been investigated [73,74]. Specifically, the titanium content in a composite coating depends on the concentration of particles in the electrolyte, current density, and duty cycle when using pulse electrolysis, and can reach approximately 11 wt.% [73]. Here, a DES (ethaline) with different loadings of titanium nanoparticles (4, 8, 16, or 32 g L^{-1}) was used. The adsorption and incorporation of titanium particles significantly altered the nucleation conditions of the nickel. Indeed, the nucleation for pure Ni originally followed a three-dimensional progressive mechanism, which then gradually shifted towards a threedimensional instantaneous model as the applied electrode potential became more negative. At the same time, the nucleation of the nickel matrix in the Ni-Ti composites corresponded to the three-dimensional instantaneous model initially but progressively ceased to obey simple theoretical models. The resulting Ni-Ti nanostructured composite films had enhanced corrosion stability, which further improved with the increase in Ti nanoparticle loading. Therefore, this approach was anticipated to produce high-performance nickel-titanium nanocomposite layers with excellent anti-corrosion performance.

The aluminum content in a composite coating deposited using an electrolyte on a DES was found to reach nearly 20 wt.% [74]. In this study, the content of Al nanoparticles in the DES-based colloidal plating baths was 4, 8, 16, or 32 g L⁻¹. The embedded aluminum nanoparticles in the DES-based plating baths facilitated the electrodeposition of Ni(II) complex ions, causing the nucleation mechanism to significantly deviate from the three-dimensional instantaneous mechanism. Nickel–aluminum composite electrodeposits revealed a slight decrease in the microhardness and anticorrosion properties compared with nickel coatings. Nevertheless, the incorporation of aluminum particulates notably enhanced the anti-oxidation ability of the composite layers. Furthermore, a high-temperature thermal treatment resulted in the formation of NiAl intermetallic and different oxides, which improved the microhardness and corrosion stability. The suggested process of Ni–Al composite fabrication is promising for the creation of anti-corrosion and high-strength surface films.

Composite coatings can be formed with a matrix not only based on "pure" individual metals but also from electrodeposited metal alloys. However, due to the apparent complexity of such processes, there have been relatively few studies in this area. In particular, a single study [75] has been published investigating the incorporation of reduced graphene oxide particles into an electrodeposited matrix of the nickel alloy NiSn (NiSn-rGO composite) using an ethaline-based electrolyte. Under pulse current conditions, high-quality NiSn-rGO composite films were cathodically deposited, exhibiting satisfactory adhesion to the copper substrate. The incorporation of graphene oxide sheets into the nickel-tim



alloy affected the patterns of surface profile, grain size, and roughness of surface. Notably, an enhancement in corrosion resistance was observed for the NiSn-rGO composites in comparison to the pure nickel-tin alloy.

Figure 11. SEM microphotographs of nickel–nano-carbon composite coatings deposited with various contents of carbon nanoparticles in solution (g/L): 0 (\mathbf{a} , \mathbf{a} ₁), 0.1 (\mathbf{b} , \mathbf{b} ₁), 0.2 (\mathbf{c} , \mathbf{c} ₁), 0.3 (\mathbf{d} , \mathbf{d} ₁), 0.4 (\mathbf{e} , \mathbf{e} ₁), 0.5 (\mathbf{f} , \mathbf{f} ₁), 0.6 (\mathbf{g} , \mathbf{g} ₁), and 0.7 (\mathbf{h} , \mathbf{h} ₁). The insets correspond to higher magnification of SEM microphotographs. Reprinted from [69], copyright 2019, with permission from Elsevier.

It should be noted that the electrochemical deposition of composite coatings from DESs that contain a metallic dispersed phase and/or a matrix not of pure metal but an alloy of multiple metals represents one of the most intriguing and promising directions. Clearly, this conclusion applies to deposited composites not only based on nickel but also based on other metals.

3.6. Cobalt-Based Composites

Electrodeposited composite films composed of a cobalt matrix with incorporated multiwalled carbon nanotubes were fabricated utilizing a reline-based deep eutectic solvent (a mixture of urea and choline chloride) [76]. The molar concentration of $CoCl_2 \cdot 6H_2O$ in the electrolytes was 1 mol L^{-1} and the content of the MWCNTs was in the range of 0.1 to 0.5 g L^{-1} . The resulting coatings of cobalt and cobalt–MWCNTs composites exhibited a uniform and smooth surface, demonstrating excellent adhesion to the Cu substrates. X-ray diffraction analysis revealed that the inclusion of MWCNTs induced a preferential orientation of metal crystallites along the (220) plane, indicating the grain refinement effect of the multiwalled carbon nanotubes. In contrast to the sharp-edged grain structure observed in pure cobalt deposits, the cobalt-based composites displayed a less dense formation characterized by relatively spherical particles interconnected by MWCNTs. It was noted that the incorporation of MWCNTs led to a reduction in the surface roughness of the electrodeposits. The corrosion resistance of the cobalt–MWCNT composite films was found to be comparable and, in some cases, slightly superior to that of pure cobalt layers, particularly evident during prolonged exposure to a 0.5 M NaCl solution. These improved

corrosion properties were attributed to the hindrance of aggressive chloride ions' diffusion by the MWCNTs.

3.7. Chromium-Based Composites

The pulse electrodeposition synthesis and characterization of chromium–single-walled carbon nanotube (Cr–SWCNT) composite coatings have been reported [77]. An environmentally safe Cr(III) plating bath was employed containing dissolved chromium chloride, choline chloride, sodium chloride, ethylene glycol, and single-walled carbon nanotubes with diameters typically below 2 nm and lengths ranging from 5 to 15 μ m. An exceptional current efficiency of approximately 70% was achieved for the Cr–SWCNT composite electroplating, representing a significant improvement compared to the typical 10%–20% current efficiency observed in industrial Cr(VI) plating baths [78]. The resulting composite coatings exhibited a uniform and crack-free surface morphology, with embedded SWCNTs forming bundles that were incorporated into the chromium metal matrix as aggregates [77]. The electroplated Cr–SWCNT composites displayed notably enhanced microhardness, measuring around 540 HV compared to the approximate 280 HV of pure chromium. Corrosion electrochemical behavior was studied in a 3.5% NaCl water solution, and the results revealed that the composite Cr–SWCNT coatings exhibited superior anti-corrosive properties in comparison to pure Cr layers.

Mejía-Caballero et al. [79] investigated the mechanisms governing the nucleation and diffusion-controlled growth of Cr nanosized particles on a glassy carbon rotating disk electrode using an ethaline-based electrolyte in which 50 mM Cr(III) ions were dissolved in the form of $CrCl_3 \cdot 6H_2O$ salt. The resulting coating, in addition to metallic chromium, also contained particles of $Cr(OH)_3$ and Cr_2O_3 compounds, thus categorizing it as a composite material. The formation of trivalent chromium oxide–hydroxide phases was attributed to the interaction with hydroxide ions, which were generated as a result of the electrochemical reduction of residual water. Consequently, the electrodeposited nanoparticles displayed a core–shell microstructure, with the core comprising metallic, zero-valent Cr and the shell consisting of trivalent chromium compounds in the form of Cr_2O_3 and $Cr(OH)_3$. Unfortunately, no physicochemical properties of the synthesized composite coating were investigated.

4. Conclusions and Possible Directions of Future Research

The electroplating of composite coatings stands as a remarkably potent and versatile technique for markedly enhancing the physicochemical and operational characteristics of surfaces, thereby imparting augmented functional properties. The scrutinized literature underscores that the electrochemical synthesis of composites facilitates the development of surface layers with heightened resistance against corrosion and wear, elevated microhardness, and distinctive electrocatalytic and photocatalytic properties. Diverse categories of plating baths can be utilized for the electrochemical deposition of composite coatings, with aqueous solutions retaining widespread usage. Nonetheless, the usage of aqueous solutions is not devoid of shortcomings; they are susceptible to aggregation and sedimentation processes, thereby compromising the stability of the bath composition and the electroplating process. One possible solution to this problem is the implementation of non-aqueous plating baths, with solutions based on deep eutectic solvents being particularly promising in this context.

Plating baths involving deep eutectic solvents present notable benefits, characterized by their environmental friendliness, ease of access, and cost-effectiveness concerning primary constituents and synthesis techniques. These baths further provide enhanced colloidal and sedimentation stability for electrolytes, facilitating the deposition of coatings featuring a diverse spectrum of precisely controlled phases and chemical compositions. Such achievements often remain elusive when employing aqueous electrolytes or plating solutions based on organic solvents. Moreover, there exists versatility in fine-tuning the properties of electrolytes based on DESs and the characteristics of the coatings deposited using these solutions. This flexibility enables precise control over the composition, structure, and properties of the coatings, ensuring tailored performance for diverse applications.

In this review, literature data on the kinetics and mechanisms of co-deposition, as well as the key operational characteristics of the composite electrodeposits obtained from DES-based plating electrolytes, were systematically examined for the first time.

Highlighting the critical avenues for future research, the exploration of the electrodeposition of composite coatings from electrolytes formulated with deep eutectic solvents necessitates attention towards the following key directions:

- Refinement of electrolyte compositions. A paramount objective lies in the meticulous adjustment of electrolyte compositions. This involves an in-depth investigation into the influence of diverse constituents within DES-based electrolytes, aiming to optimize their composition for the enhancement of composite coating properties.
- 2. Investigation of nanoparticle size effects. Establishing discernible patterns concerning the impact of nanoparticle sizes assumes significance. It is imperative to delve into the effects of varying sizes of nanoparticles within the dispersed phase on the kinetics and inherent properties of electrochemically deposited composite coatings. This avenue of research should provide insights into the interaction between nanoparticle dimensions and the resulting coating characteristics, paving the way for tailored coatings with precise functionalities.
- 3. Exploration of co-deposition mechanisms. A thorough investigation into the electrode-position mechanism is essential to the advancement of knowledge in this field. This involves a comprehensive exploration of the interactions between the electrochemical processes, adsorption kinetics at the electrode surface, and the resulting microstructure and chemical composition of composite coatings. Such in-depth studies should reveal the underlying mechanisms governing the formation of these coatings, offering insights into optimizing the deposition process for enhanced performance.
- 4. Analysis of colloidal-chemical behavior of DES-based electrolytes. A crucial aspect of future research involves establishing clear patterns in the colloidal-chemical behavior of suspensions and colloidal electrolytes formulated with DESs. These electrolytes are pivotal for the electrolytic deposition of composite films. The goal is to develop more stable and reliable technological processes tailored for practical applications. Understanding the behavior of these systems at a molecular level will enable the fine-tuning of deposition parameters, leading to improved coating quality and durability.
- 5. Utilization of advanced characterization techniques. The application of advanced characterization methods, such as in situ monitoring or real-time imaging, holds particular significance for a comprehensive understanding of the evolution of composite coatings during electrodeposition. These cutting-edge techniques should offer invaluable insights into the dynamic processes occurring at the electrode interface, allowing for precise observations of morphological changes, phase transformations, and surface interactions in real time. Such detailed analysis will aid in elucidating the mechanisms governing the formation of composite coatings, thereby paving the way for optimized deposition strategies and enhanced coating properties.
- 6. Identifying pathways for the flexible control of process parameters. This involves the identification of pathways for flexible control over process parameters. Specifically, it is of great value to delve into the effects of various parameters such as temperature, stirring rates, current densities, and different current regimes on the deposition kinetics and resultant properties of composite coatings. By systematically varying these parameters and analyzing their impact on coating morphology, composition, and performance, optimized process conditions tailored to specific application requirements could be established. This endeavor should aim to uncover the interactions between process variables and coating characteristics, facilitating the development of advanced and adaptable electrodeposition techniques for composite coatings.
- 7. Tailoring specific composites for targeted applications. A pivotal focus for future research lies in the development of tailored composites designed for specific appli-

cations. This involves meticulous adjustments to the composition, structure, and properties of coatings to align with the requirements of distinct end-use scenarios. Of notable promise and significance is the advancement of high-performance, reliable electrocatalysts tailored for use in green hydrogen energy applications. By fine-tuning the characteristics of these coatings, researchers aim to enhance efficiency, durability, and overall performance for sustainable energy processes.

- 8. Integration of environmental and economic considerations. It is imperative to incorporate mandatory evaluations of environmental sustainability and economic feasibility. This aspect holds particular weight when employing DES-based electrolytes, necessitating the exploration of eco-friendly and cost-effective approaches. Understanding the environmental footprint and economic viability of these processes ensures the development of sustainable practices that align with global initiatives towards greener technologies.
- 9. Exploration of multi-elemental and multi-phase composite deposition. A promising frontier emerges in the field of multi-elemental and multi-phase composite deposition. This direction extends the research horizon to encompass the simultaneous deposition of multiple elements or compounds within composite coatings. This innovative approach not only expands the range of functionalities but also offers enhanced versatility and performance in various technological applications.

Funding: This research was funded by the Ministry of Education and Science of Ukraine, grant number 0124U000563.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The data presented in this study are available upon request from the corresponding author. The data are not publicly available due to technical limitations.

Conflicts of Interest: The author declares no conflicts of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript; or in the decision to publish the results.

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Article



Combined Terahertz Pulsed Imaging and Optical Coherence Tomography Detection Method for Multiple Defects in Thermal Barrier Coatings

Manting Luo ^{1,*}, Shuncong Zhong ^{2,3}, Yi Huang ^{2,3}, Zhenghao Zhang ^{2,3} and Wanli Tu ⁴

- ¹ School of Mechanical Electrical and Information Engineering, Putian University, Putian 351100, China
- ² School of Mechanical Engineering and Automation, Fuzhou University, Fuzhou 350108, China;
- zhongshuncong@hotmail.com (S.Z.); yihuang@fzu.edu.cn (Y.H.); 200210006@fzu.edu.cn (Z.Z.)
- ³ Fujian Provincial Key Laboratory of Terahertz Functional Devices and Intelligent Sensing, Fuzhou University, Fuzhou 350108, China
- ⁴ Marine Engineering Institute, Jimei University, Xiamen 361021, China; wanlitu@163.com
- * Correspondence: mantingluo163@163.com

Abstract: While thermal barrier coatings (TBCs) are being sprayed onto aero-engine turbine blades, or while the engine blade is working, high temperatures and strong impact forces will damage TBCs under thermal cycles, resulting in the coating peeling off from the blades. The current method of using ECT, IRT, or another method alone cannot achieve the real-time detection of coating defects with both high precision and high penetration power. Two detection methods, namely, terahertz pulsed imaging (TPI) and optical coherence tomography (OCT), were combined to evaluate typical defects observed in TBCs (including internal debonding cracks, surface high-temperature cracks, and surface etched cracks). The results showed that the OCT system successfully obtained the micron-level axial resolution, but the detection depth of the OCT system was limited. The TPI system achieved a higher penetration depth than OCT-hence, it can be used for the nondestructive detection and evaluation of the internal debonding defects in the sample-but its resolution needs to be improved. Following this conclusion, a method is proposed using TPI and OCT concurrently for the nondestructive testing and quantitative evaluation of TBCs on etched cracks, thus achieving progress both in terms of depth and resolution. In our experiment, defects with a depth of 519 µm and a width of 100 µm were measured. The proposed method is suitable for situations where multiple defects in TBC samples of blades need to be detected simultaneously during the working process. When there are defects deep inside the sample, more small cracks on the surface can be evaluated to achieve a combination of depth and accuracy.

Keywords: thermal barrier coatings; defects detection; terahertz pulsed imaging; optical coherence tomography; depth; resolution

1. Introduction

As the core component of the aircraft, the engine works at an internal temperature of more than 1600 °C and even up to 2000 °C during operation [1]. Therefore, the blades of the engine need to be made of special materials, which can withstand high temperatures and high pressure and have good stability. Thermal barrier coatings (TBCs) on the aeroengine turbine blades are an important factor in improving the operating efficiency of the engine [2,3]. As shown in the following picture, Figure 1a is a turbine engine, Figure 1b is the blade of a turbine engine, and the typical structure of the thermal barrier coatings is shown in Figure 1c [4], which consists of super alloy, bond coat (BC), and ceramic layer (Topcoat, TC). The propagation of microcracks on the TC layer and the thickening of thermally grown oxide (TGO) caused by oxidation at high temperatures are the main factors causing the failure of TBCs [5]. At present, the most frequently used method for failure

Citation: Luo, M.; Zhong, S.; Huang, Y.; Zhang, Z.; Tu, W. Combined Terahertz Pulsed Imaging and Optical Coherence Tomography Detection Method for Multiple Defects in Thermal Barrier Coatings. *Coatings* 2024, 14, 380. https://doi.org/ 10.3390/coatings14040380

Academic Editors: Jose Maria De Teresa, Ricardo Lopez Anton and Sion Federico Olive Méndez

Received: 19 February 2024 Revised: 15 March 2024 Accepted: 20 March 2024 Published: 24 March 2024



Copyright: © 2024 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). detection is using a scanning electron microscope (SEM) to obtain the section information of TBCs under static conditions. However, it is a destructive testing method and cannot conduct real-time detection.



Figure 1. Structure of the thermal barrier coating. (a) Turbine engines. (b) Turbine engine blades. (c) Thermal barrier coating structure [4].

Nondestructive techniques for the detection of defects in samples mainly include ultrasonic testing (UT), eddy current testing (ECT), X-ray detection, infrared thermography (IRT), and so on. Among them, ultrasonic testing methods have developed rapidly in recent years. When ultrasound is propagated to the inside of the sample through the coupling agent, the internal defects will hinder its propagation, while the ultrasonic propagation remains unchanged in the position without defects [6,7]. However, it requires contact with the sample at the time of measurement, and the TBCs have many pores, so ultrasonic testing is not suitable for TBCs. Eddy current testing technology mainly detects different eddy current amplitudes and alternating phases generated by different objects moving under the interaction of various alternating phase magnetic fields [8], which is easily affected by material conductivity, sample size, and shape. X-ray detection has the problem of unignored energy radiation; it needs to be isolated and protected when conducting experiments, thus resulting in the limitation of the sample testing environment. At present, the detection resolution of the infrared thermography method needs to be improved, and the penetration ability of samples is insufficient [9–11], so the research on this detection method needs more exploration. Up to now, no nondestructive testing method can fully and accurately detect the characteristics of all TBC systems. Therefore, the advantages of different detection methods should be used for the comprehensive evaluation of TBCs. Li Jianchao et al. [12] reviewed the detection capabilities of different methods of TBC testing, such as UT [7,13], ECT [14], X-ray [15,16], and IRT [17,18]. The detection capabilities of different nondestructive testing TBC methods are summarized in Table 1.

In our work, other two methods were used to evaluate thermal barrier coating defects. The first method was terahertz pulsed imaging (TPI). Terahertz wave is a kind of electromagnetic radiation with a frequency of 0.1~10 THz, which can be used to detect nonpolar objects [19]. TPI has become a new method with great potential in TBC measurement, offering a high signal-to-noise ratio and high detection depth [20]. At present, TPI is used to detect the thickness of TBCs [21], but the thin TGO layer beyond the resolution limit cannot be examined. In terms of pore growth, the tendency for variation in terahertz properties of YSZ ceramic coatings with different microstructure features (porosity, pore-to-crack ratio, pore size) was investigated [22]. The electromagnetic wave transmittance and dielectric properties of thermal barrier coatings, as well as the evolution of defects at the interface of oxide, ceramic, and metal layers [23,24], have been studied, and research is increasingly being devoted to the issues of terahertz peak aliasing and resolution limits that cannot be exceeded. The internal debonding and surface-etched cracks were measured in our experiment to achieve the nondestructive evaluation and prediction of process failure in TBCs. The other method that has been used is optical coherence tomography (OCT), which adopts the principle of near-infrared light interference and can obtain a high resolution

of 5 to 15 μ m [25]. Due to significant absorption and strong scattering of near-infrared light in thermal barrier coatings, only surface cracks in thermal barrier coatings can be detected. With its micron-level high resolution, OCT serves as a valuable tool for the auxiliary detection of defects and detailed features in samples. Currently, OCT detection in TBCs primarily focuses on coating thickness and surface defects instead of internal defects [26,27]. This paper proposes a method for the nondestructive testing and quantitative evaluation of thermal barrier coatings by combining TPI and OCT, leveraging the complementary advantages of both techniques. The resolution and penetration depth of these two methods were evaluated to assess their effectiveness.

NDT	Detection	Conclusions			
	Density	Succeeded in evaluating the coating density of varying thicknesses from 0.16 mm to 0.48 mm.			
UT	Thickness	The thickness of YSZ coating (256–330 μ m) sprayed by plasm on the 1Cr18Ni9Ti matrix was measured. The absolute error range between the measurement results and the metallograph observation results is $\pm 10 \ \mu$ m, and the relative error range is $\pm 3\%$.			
	Bond quality of TBCs	Could detect 0.2–2.0 mm length of debonding.			
ECT	Large internal coating pores, the remaining thickness of the top layer of the ceramic, and its remaining life	Completed the detection of the (1) TC layer with a thickness of 244 μ m, with an error of 1.4%; (2) thickness and conductivity of bond coating to detect delamination.			
	Measurement of phase evolution	Studies of phase evolution are performed by X-ray diffraction (XRD) and by evaluating the intensities of a few diffraction peaks for each phase.			
X-ray	Strain response	Hollow cylindrical specimens, with larger temperature drops across the coating, and significant strain gradients are seen, which can contribute to failure modes occurring within the layer adjacent to the interface.			
	Coating thickness	The thickness of nonuniform TBCs was detected, and the results showed that the pulse imaging accuracy was 0.3~2.3 $\mu m.$			
IRT	Coating defects	Monitors the development of specific failure modes, such as coating delamination after various thermal cycles, utilizing the thermal wave amplitude signals.			
	Debonding of samples	Validation tests indicated that blind holes with diameters of 1, 2, and 3 mm and artificial disbonds with diameters of 2 and 3 mm in TBCs are detected.			

Table 1. Detection ability of different TBCs nondestructive testing methods.

2. Methods and Materials

It is vital to identify engine blade defects as early as possible to prevent the devastating damage caused by aviation accidents. The thermal stress and expansion coefficient differences between the TC on the surface of TBCs and the substrate can lead to thermal stress loss and mismatch in the metal substrate during service. This can result in surface cracks in the TC layer [28], internal debonding, and the growth of a TGO layer, ultimately leading to the failure of the thermal barrier coatings [29].

2.1. Methods

The TPI method was first applied in this experiment. When a TPI system is utilized for quantitatively detecting defects in coatings, any defects can lead to changes in the shape of the terahertz detection waveform [30]. As a result, the terahertz method can be employed effectively for the early diagnosis of defects. The terahertz system contains transmission mode and reflection mode, and a diagram of the reflection mode we used in the experiment

is shown in Figure 2a. Figure 2b shows the Terapulse 4000 (TeraView (Cambridge, UK)) we used in this work, where the central wavelength of the laser is 800 nm, and the repetition rate is 80 MHz. The principle of a terahertz system is as follows [31].



Figure 2. TPI system. (a) Diagram of the TPI system [31]. (b) Terapulse 4000 (TeraView) used in the experiment.

By changing the delay of the pump pulse in the terahertz system, the sampling value of the detector changes, and a probe pulse is used to measure the terahertz-induced transient response in the detector. The electric field E(t) of the terahertz pulse is recorded as a function of the delay time. The information of the electromagnetic pulse $\tilde{E}(w)$ in the frequency domain can be obtained by the Fourier transform of the time domain pulse, expressed as [32]:

$$\widetilde{E}(w) \equiv A(w) \exp[-i\phi(w)] = \int_{-\infty}^{+\infty} E(t) \exp(-iwt) dt,$$
(1)

In the equation, A(w) is the amplitude and $\phi(w)$ is the phase of the terahertz pulse. Once the electric field of the terahertz pulse is recorded, the Fourier transform can be performed to obtain the amplitude and phase of the pulse. In a system, the time range *T* of time-domain waveform measurement is related to the spectral resolution δ_w of the terahertz time-domain spectrum, and the time resolution δ_t of waveform measurement is related to the spectral range Ω . The relationship between them is as follows:

$$\delta_w = 2\pi/T, 2\Omega = 2\pi/\delta_t,\tag{2}$$

The coating thickness can be calculated using the following formula [33]:

$$d_i = c(\Delta t_i - \Delta t_{i-1}) \cos \theta / (2n_{coating}), \tag{3}$$

where d_i is the thickness of the measured coating (i = 1, 2, 3...), Δt_i represents the time delay between the reflection peaks of the TPI detection signals at each coating interface [34], and $\Delta t_0 = 0$. $\cos \theta$ is the cosine of the refraction angle, and because $\theta = 0^\circ$, $\cos \theta = 1$. $n_{coating}$ is the refractive index of the material being measured. In our previous work [23], a signal analysis was carried out on the same sample used in the etched cracks in Section 2.2.3 during SWT processing of the signal, and it was found that the refractive index of the sample concurred with the conclusion that the refractive index of the TC layer of TBCs was 4.7, as established in [35]. Therefore, the refractive index of the TC coating is set as 4.7 in our experiment when calculating the depth of the etched crack.

In addition, detailed information on the structure of the TBC sample can be detected in conjunction with the OCT system. The principle of OCT can be described as "ultrasonic imaging in optics", which can achieve the tomography of the internal microstructure of a sample. In an OCT system, light from an optical source is split into two paths, a sample path and a reference path. Light in the reference path is reflected from a mirror (RM) whereas light in the sample path is reflected from surface and subsurface features of the ceramic samples (S). The reflected light from the sample path will only be detected if it travels a distance that closely matches the distance traveled by the light in the reference path—this constraint incorporates depth resolution into the technique [36]. The biggest advantage of the OCT system is that its resolution can reach the micrometer level. The schematic diagram of the OCT system is presented in Figure 3a [37]. Figure 3b is the Ganymede-II (Thorlabs (Newton, NJ, USA)) we used in the work; the central wavelength of the light source is 930 nm, and the axial resolution in the air is 6 µm.



Figure 3. (a) Diagram of OCT system [37]. (b) Ganymede-II (Thorlabs) used in the experiment. SLD: super luminescent diode; C1: collimator 1; C2: collimator 2; FC: fiber collimator; S: sample; RM: reference mirror; G: grating; Cyl: cylindrical lens; LSC: linear camera.

When the reference light interferes with the sample light, the OCT system in the frequency domain can obtain complex envelope information in the depth direction of the samples. Among them, the interference light spectrum signal in real form can be represented as [38]:

$$I_{real}(\mathbf{k}) = S(k) \left(a_R^2 + 2 \int_{-\infty}^{\infty} a_R a(z) \cos(2knz) dz + \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} a(z) a(z') e^{i2kn(z-z')} dz dz' \right), \quad (4)$$

where S(k) represents the power spectrum distribution of the light source, a_R represents the reflection coefficient of the reference mirror, a(z) represents the reflection or scattering coefficient of the different depth layers of the sample, n is the refractive index of the sample, and k is the wave number ($k = 2\pi/\lambda$). a(z) can be obtained by FFT transformation on the interference spectrum signal $I_{real}(k)$.

$$FT^{-1}[I_{real}(\mathbf{k})] = FT^{-1}[S(k)] \otimes \left(a_R^2 \delta(z) + 1/2a_R \hat{a}(z) + 1/8AU[\hat{a}(z)]\right),$$
(5)

where a(z) = a(z) + a(-z), \otimes represents the convolutional operation, AU[a(z)] represents the represent autocorrelation function, and the symmetric distribution of a(z) can be obtained from the above equation a(z), further obtaining a(z).

2.2. Sample Preparation

Tests were carried out on some samples with thermal barrier coating defects such as internal debonding cracks, surface high-temperature cracks, and surface etched cracks, which often occur in the process of blade work. We describe in detail the preparation process of three different samples, with their ceramic coating being deposited onto components via air plasma spray (APS). The detection target of this experiment was a method that could conveniently detect the occurrence of multiple cracks in the same sample.

2.2.1. Internal Debonding Cracks

During the TBC spraying process or while the engine blades are in operation, the difference in thermal expansion coefficients between the TC layer, BC layer, and TGO layer at high temperatures can cause the original bonding effect between the TC and BC layers to transform into thermal mismatch stress, resulting in the detachment of TBCs and exposure of the substrate to high-temperature gases, further causing serious consequences. The production process of the sample with internal debonding cracks in Figure 4 includes three steps. The TBCs are composed of a plasma-sprayed zirconium dioxide (ZrO₂) TC layer, BC layer, and nickel-based alloy substrate. The Ni-based alloy substrate size is $50 \text{ mm} \times 40 \text{ mm} \times 2 \text{ mm}$, thread through a hole (debonding defect) with a diameter of 2 mm and 3 mm, a base thickness of 5.82 mm, and a TC layer thickness of 281 μ m. First, a threaded hole the size of a TC-BC debonding defect was tapped on the alloy steel, and the matched screw was tightened. Then, the screw head was cut off above the base, and the top surface of the screw was polished. In the following step, mechanical shot peening was carried out on the surface to achieve the preparation of the plastic surface of the component. Finally, the TC layer was sprayed on the upper surface of the component. When the sample had cooled, the screw was loosened to a suitable distance (the distance was smaller than the alloy substrate) to form an air layer to simulate the debonding defects in the sample. As the clearance between the screw and the substrate was small enough to exceed the detection limit of the terahertz pulse, it was regarded as an integral part of the substrate. The sample was prepared with the help of the Beijing Institute of Technology. Figure 4a,b shows the front and backside diagrams of the sample with debonding defects, and Figure 4c is the cross-sectional view of the sample. The two defects are located at different positions on the diagonal of the sample, which makes it convenient to distinguish and coordinate the positioning in the following detection.



Figure 4. Diagram of the TC debonding sample. (**a**) Front diagram of the sample with debonding defects between TC layer and base. (**b**) Backside diagram of the sample with debonding defects between TC layer and base. (**c**) Cross-sectional view of the sample.

2.2.2. Surface High-Temperature Cracks

Under the action of working cycles at high temperatures, a large thermal mismatch and corrosion stress exist during service [39]. Due to the phase transition or local sintering of ceramic materials, the surface of the ceramic will shrink. When the internal stress is larger than the limit of the ceramic material, cracks will occur [40]. If the crack area becomes too large, it will cause the ceramic layer to peel off and, thus, greatly reduce the service life. The second type of sample we prepared was a high-temperature oxidation defect sample, a diagram of which is shown in Figure 5a. The production process was as follows (the sample was prepared with the help of the East China University of Science, and we performed the additional heat treatment): The sample was a three-layer structure, including a metal substrate, BC layer, and TC layer. The size of the alloy steel substrate was $\phi 25 \times 3.1$ mm. The ceramic layer material of this sample was yttrium oxide partially stabilized zirconia (8YSZ). The ceramic coating was a powder of 45–96 µm in size, and the thickness of the ceramic coating was about 250–300 μ m. The sample was gradually heated to 1100 °C in the heat treatment furnace and held for 40 h of high-temperature oxidation. Then, the sample was cooled in air at a standard pressure from 1100 °C to 10–20 °C. The cooling time was 36 h and the cooling rate was 30 °C/h. Due to the larger particle size, there was greater stress between the layers, and elongated cracks appeared on the surface of the sample during cooling. The cracks were detected under the metallographic microscope and TPI system in normal environmental circumstances. The holes were discontinuous, and the cracks' size was between 20 and 60 μ m as can be seen in the metallographic micrograph in Figure 5b.



Figure 5. A sample with surface high-temperature cracks and its metallographic micrograph. (a) The diagram of the high-temperature oxidation sample, and the box position is the location of the crack. (b) Photographs of cracks under a metallographic microscope.

2.2.3. Etched Cracks

The last type of sample contained the etched cracks. The base material of the TBC sample was a nickel-based superalloy block material (brand DZ125) cut into small test pieces (size 30 mm \times 10 mm \times 2 mm) using wire. The metal bonding layer material was nickel-based high-temperature alloy powder. The ceramic layer material was yttrium oxide partially stabilized zirconia (8YSZ). Cracks of different widths and forms were carved on the surface of the TC layer by laser etching to simulate the failure condition of the sample under a strong impact force. This type of damage is usually due to mechanical damage or a sudden impact. Two differently structured TBC samples are shown in Figure 6a,b; the TC layer thickness of sample Figure 6a is about 500 µm, and the TC layer thickness of sample Figure 6b is 265 µm. In the figure, the grooves mark the positions of the samples. The three widths are 100 µm, 200 µm, and 300 µm, respectively, and the depth is 200 µm in all three cases.



Figure 6. Diagram of the etched crack. (a) Sample A with 100 µm and 200 µm width cracks. (b) Sample B with 300 µm width cracks.

3. Experiment

TPI and OCT nondestructive testing of different defect samples (such as containing internal debonding cracks, surface high-temperature cracks, and surface etched cracks) were conducted to compare their detection capabilities.

3.1. OCT and TPI Penetration Ability Experiment

3.1.1. Samples without Defects

First, two TBC samples with different TC layer thicknesses were tested under the same spraying conditions on a metal base to evaluate the penetration ability. A frequency-domain OCT system was used to detect the TC layers where the thicknesses were 180 μ m and 280 μ m. Under the same scanning parameters, the one-dimensional OCT waveforms of the two samples are shown in Figure 7a. Since one-dimensional OCT signals adopt a B-scan in the *x*–*z* direction, the depth information of samples can be obtained directly from images. It can be seen that the penetration capacity of the OCT system for ceramic coatings of different thicknesses is almost the same, but we could not find the difference between the 180 μ m and 280 μ m samples. In addition, the boundary between the TC and the metal base cannot be detected. This is because the top YSZ of the TBCs is a pore structure, and the SLD light source of OCT has insufficient penetration ability and a strong scattering effect in the pores; hence, the backscattered light that characterizes the sample information collected by the system is weak. Therefore, the detection depth of the OCT system is insufficient.



Figure 7. (a) One-dimensional waveforms of the sample without defects measured by the OCT system. (b) Time domain pulse signals of 180 µm and 280 µm samples using the TPI system.

The one-dimensional signals of two different coating samples measured using the TPI system are presented in Figure 7b, and the locally amplified signals are shown in the box area. We could see that there is a significant difference in the signals of the two different thickness coatings. The reflection wave of a coating with a thickness of 180 μ m occurs earlier than that of 280 μ m. The interface stratification can be obtained from the one-dimensional diagram, and thus, we can verify the TC thickness through Formula (3).

The results show that the TPI system has better penetration ability than the OCT system. OCT systems can only detect thermal barrier coatings no thicker than 200 μ m, which has been confirmed both in experiments and the literature [36]. The TPI system in this experiment penetrated the thermal barrier coatings above 280 μ m and even deeper.

3.1.2. Samples with Internal Debonding Cracks

Furthermore, the debonding defects inside the sample (Figure 4) were prepared to emphasize the penetration ability of the TPI system on the TBCs. As the OCT system could not penetrate the 280 μ m TC layer, it was unable to complete the detection of debonding defects.

The TPI two-dimensional C-slice peak-peak imaging of the detected samples is shown in Figure 8a. The outer circular is the shape of the sample table fixture for the TPI system. Occluded by the fixture table, the sample outside the circular shows a black shadow signal under detection. From the two-dimensional image, the position and size of the 2 mm or 3 mm artificial debonding defects can both be observed. We can realize the location of the defects according to the relative position of the fixture table and the sample.



Figure 8. (a) Terahertz 2D C-slice peak-peak imaging of debonding defect samples. (b) Onedimensional time-domain waveform of 11 positions in the y-direction of 3 mm defect position.

Terahertz time-domain waveforms of 11 position points in the same x-direction with different y-direction values (dashed line direction in Figure 8a) at the defect location of 3 mm were extracted, and 11 waveform signals were made continuously on the data graph for comparison, as shown in Figure 8b. It can be seen that the position of the debonding defect is also the position of the red terahertz waveform in Figure 8b—the signal has evident deformation, and the peak-to-peak value becomes smaller. In the *y*-axis position, the deformation waveform can be obtained within the range of the defect size of 3 mm. Due to the small size of the air gap within the defect, the reflected waveforms before and after the air gap at the debonding position cannot be temporally distinguished. The shape of the reflected waveforms differs from the original incident waveforms, indicating the presence of defects after the terahertz wave passes through the detected object.

It can be concluded that the TPI system can realize the quantitative detection of the debonding defects even inside the sample with a diameter larger than 2 mm, and we can distinguish both 2 mm and 3 mm defect locations in the image. Hence, it was confirmed here once again that terahertz waves have a stronger penetration ability than infrared light sources in OCT systems.

3.2. Resolution Ability Experiment of OCT and TPI

3.2.1. Surface High-Temperature Cracks

In this experiment, high-temperature oxidation defects on the surface of the sample (Figure 5) were detected to test the resolution of the OCT system.

Three-dimensional imaging was used to analyze more detailed information. As shown in Figure 9a, the red box is the sample detection range. It is not appropriate to set the scanning range to be too large concurrently with a small step size; otherwise, the storage memory will overflow. We set the detection range as $0.6 \text{ mm} \times 1.12 \text{ mm} \times 1.5 \text{ mm}$ in the experiment; the detection resolution was $2 \mu \text{m} \times 2 \mu \text{m} \times 2.04 \mu \text{m}$; the acquisition time (3D) was about 3 min; and the data storage and imaging time was about 2 min. Figure 9b is the *x*-*y* section diagram near the focal point of the 3D OCT image of the sample, and the approximate position and width of the crack can be seen in the white arrow and square in the figure. Due to the existence of an air gap at the crack location, the refractive index is lower than that of other coating components, so the color of the position indicated is dark and its backscattered light is weak. Figure 9c is the crack location also presents a low

backscattering region different from the normal location in the depth direction. In the figure, the depth of the crack can be evaluated according to the coordinates of defects in the *z*-direction. Therefore, combining with the sample signals of different sections, the location and quantification of sample cracks can be realized. The crack width of this sample is about $35 \,\mu\text{m}$.



Figure 9. Scanning images of high-temperature oxidation cracks. (a) The picture of the high-temperature oxidation crack on the OCT sample table; the red box is the scanning area of the picture. (b) x-y cross-section near the focal point of 3D OCT imaging of the sample. (c) y-z cross-section of a location for volume standard OCT imaging of the sample.

There are no TPI images as the resolution is insufficient to produce worthwhile measurements. The main reason is that the terahertz beam after collimation is above 100 μ m, which limits the lateral resolution of the TPI system. As the OCT system has a higher detection resolution, it can obtain better results in shallow surface imaging, thus showing its advantages. On the other hand, to collect more detailed information, the OCT system needs to set a shorter scanning step and collect more sample data points, which may take more time. Therefore, OCT is more suitable to be an auxiliary means of detecting TBC samples.

3.2.2. Etched Cracks

The mechanical damage cracks were simulated by creating artificial etched cracks (Figure 6), and then, both systems were simultaneously used to detect them. First, the sample was detected by TPI, with the detection range of the system set as 14 mm \times 14 mm and 18 mm \times 10 mm, the scanning step as 200 μ m, and the detection time as 5 min.

The size and location of the 100–300 μ m crack can be obtained from the TPI twodimensional C-slice diagram in Figure 10.



Figure 10. Diagram of two samples with surface cracks etched in different directions and widths. (a) Two-dimensional imaging of TBCs with horizontal cracks etched: the two cracks etched are 100 μ m and 200 μ m. (b) Two-dimensional imaging of TBCs with mixed direction cracks etched: all cracks etched were 300 μ m.

One-dimensional waveforms were also extracted from the surface crack data of 100 µm and 200 µm in Figure 10a, and then, the waveform changes were compared in Figure 11a. It can be seen from the figure that the larger the defect width, the smaller the TPI signal strength. When the width of the defect is 200 µm, the surface reflection terahertz timedomain signal of the crack is at its weakest. The terahertz waves are scattered within the groove of the etched crack, resulting in a decrease in the returned terahertz intensity. At the same time, with the increase in the width of the defect, the waveform shifted backward and deformed. When the width of the defect was 200 µm, a second terahertz reflection peak appeared, and the depth of the artificial crack could be calculated as 266 µm according to the flight time of the two terahertz reflection peaks. However, when the defect width is 100 µm, it is quite difficult to distinguish the waveform change in the defect due to the resolution limit of the TPI system and the superimposed terahertz waveform. In addition, we observed that the reflection peak in the dashed elliptical box was the bottom of the TC layer, and the thickness of the TC layer was 519 µm, which was consistent with the sample parameters. Then, we performed a spectrum transformation for one-dimensional signals at different positions with different widths, as shown in Figure 11b. The defect information of the sample can be obtained when observing only the magnitude of the electric field in the frequency domain. The frequency domain electric field intensity at 100 µm is slightly decreased and barely recognizable, and when the defect size reaches 200 µm, the spectral absorption peak caused by the defect structure is quite significant. The frequency at which the minimum intensity is located indicates the corresponding defect width.



Figure 11. (a) One-dimensional time-domain signals for the positions without defects and signals for the positions of etched cracks with different widths. (b) One-dimensional frequency-domain signal of etching crack positions without defects and with different defect widths.

It can be seen from the one-dimensional time-domain/frequency-domain waveform and two-dimensional image of the sample that the TPI system can easily realize the detection of laser etching cracks on the surface of about 200 μ m width.

The B-slice cross-sectional diagrams (with and without defects) at different positions of the 300 μ m defect ("+" shape) sample in Figure 10b are compared as follows (Figure 12). The *x*-coordinate is the scanning position of the high-precision linear platform, and the *y*-coordinate is the optical delay line of the system. It can be seen from Figure 12b that in the depth direction, there is an extra reflection interface. In a partially enlarged image in Figure 12b, the terahertz reflection wave at the bottom of the etched crack is represented by the arrow at position 1. In addition, TPI can simultaneously detect the total thickness of the TC layer (arrow 2).



Figure 12. B-slice cross-sectional imaging of normal and defective locations on the etched crack sample. (a) B-slice cross-sectional imaging of the normal location on the etched crack sample. (b) B-slice cross-sectional imaging of the defect location on the etched crack sample.

The OCT system was also used to detect the surface "+"-shaped etched crack samples (Figure 6b), and the detection range and accuracy were compared with TPI. As mentioned before, the crack width was about 300 µm. The detection range was set to 1.5 mm \times 1.7 mm \times 1.5 mm, with a detecting resolution of 3 μ m \times 3 μ m \times 2 μ m. The imaging time (3D) was about 3 min. The sample pictures and OCT detection results are shown in Figure 13. Figure 13a is the actual photo of the sample, and the red area indicates the scan range. When the area becomes larger, the data points become larger, thereby increasing the imaging workload. Figure 13b is the three-dimensional OCT imaging of the sample (surface imaging only), from which the width and depth of the manufactured crack can be seen, and circular grooves formed by repeated etching can be seen at the intersection of the two crack centers, as indicated by the white circle and arrow marks in the figure, which are not detectable in TPI imaging. Figure 13c is the volume standard imaging, in which the three-dimensional structure information of the sample can be seen more intuitively and reliably. The black part of the surface in the image is the etched crack. Figure 13d is the x-z direction of the volume standard imaging where the bottom of the sample groove has stronger interfacial reflection than the air, which represents the depth information of the sample groove. We can achieve the depth information of the surface crack, as indicated by the distance *d* shown in Figure 13d.



Figure 13. (a) The picture of the surface etched crack on the OCT sample table; the red box is the scanning area of the picture. (b) 3D OCT imaging of the sample (surface imaging only). (c) Volume standard imaging of the sample. (d) An *x*-*z* cross-section of a 300 μm etched crack at a certain location.

Furthermore, Figure 14a shows the one-dimensional TPI signals of the 300 μ m etched crack, and Figure 14b shows the OCT detection signals of the same crack.



Figure 14. TPI one-dimensional signal and OCT one-dimensional signal of surface etched "+"-shaped crack samples. (a) TPI signals of etched cracks. (b) OCT signals of etched cracks.

As can be seen from the figure, although the light intensities of the two signals are quite different from each other, the one-dimensional signals of both show the reflected crest position of light waves at the layered interface of the sample. The distance *d* of the interface can be obtained, being the depth of the defect. In addition, the waveform and the peak characteristics of the two figures are quite different. As can be seen, the TPI signals have stronger signal intensity with a better signal-to-noise ratio and smoother waveform. The detected TPI signals reveal multiple reflection echoes between the interlayer boundaries of the sample, suggesting penetration through ceramic coating samples of significant thickness beyond the metal bond coat layer and substrate. However, in the one-dimensional OCT image, the backscattered signal intensity from detectors appears weaker, with insufficient depth of penetration due to the strong scattering effect of the ultra-radiant light source in the ceramic gap and its relatively weak intensity.

Last, the widths of the defects at 100 μ m and 200 μ m, measured using TPI, OCT, and metallographic microscopy, are compared in Table 2. The width of each defect was measured three times, and the average value was obtained. One of the reasons considered to explain the measurement error of the crack width in both OCT and TPI systems is the error in setting the refractive index of the TC layer. Due to the influence of different spraying conditions and structural parameters on the refractive index of TBCs, the optical path length (*nd*) can be used to verify the measurement accuracy of the samples when comparing OCT and TPI results.

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lable 2. Mean	thickness	comparison	of IPI, OC	$_1$, and MM ¹ .	

	Resolution	Thickness of the TC Layer	Crack 1# Width (100 μm)	Crack 2# Width (200 μm)	Characteristic of Method
TPI	~100 µm (lateral) 30 µm (axial)	519 µm	Hard to detect	253 μm	Real-time, nondestructive
OCT	5–15 µm (axial)	Not detected	121 μm	244 µm	Real-time, nondestructive
MM	0.2–0.5 μm	Need to be cut and polished	115 µm	221 µm	Damaged, in vitro

¹ MM: Metallographic microscope.

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The results showed a good resolution advantage of using the OCT system because it is closer to achieving the measurement results of a metallographic microscope, which has the highest resolution. When the defect width is 100 μ m, the relative error between the two methods is 5%, and when the defect width is 200 μ m, the relative error is 10%. However, the disadvantage is that we cannot detect the bottom of the TC layer, that is, we cannot know the actual thickness of the TC layer.

We further analyzed the width of defects measured by TPI, OCT, and MM methods at $100 \mu m$, $200 \mu m$, and $300 \mu m$ (see Figure 15).



Figure 15. (a) The mean value and standard deviation of width measurements using three methods for detecting defects at 100 μ m, 200 μ m, and 300 μ m. (b) The relative errors of TPI, OCT, and MM methods for measuring defects at 100 μ m, 200 μ m, and 300 μ m with respect to the mean values.

The mean value and standard deviation of three methods for detecting the width of three defects were calculated as shown in Figure 15a. The average values were 118 μ m, 239 μ m, and 337 μ m, respectively. The minimum standard deviation is 4.2 μ m when measuring 100 μ m defects. Figure 15b shows the relative errors of TPI, OCT, and MM methods for measuring defects at 100 μ m, 200 μ m, and 300 μ m with respect to the mean values. (The TPI method's values of 100 μ m cracks were omitted because they could not be detected). The results measured by OCT and MM are closer to the mean value of the three methods; however, due to the higher resolution of the MM method, we still used the measurement results of MM as a reference value in this experiment. In addition, the resolution provided by OCT is higher than that of TPI, whose detection value is closer to the MM method and its mean value.

In conclusion, OCT signals can detect the repeated etched grooves at defect intersections and complete the 100 μ m defect detection in this experiment on etched cracks. This demonstrated a higher detection accuracy, and thus, it was superior when the crack depth was shallower. The experiments show that the scanning range of OCT is limited compared with TPI, and the data storage is more complex. Defect measurement can be accomplished at the micron level, but the detection depth is insufficient. TPI obtained the width and depth of the 200 μ m crack, as well as the total thickness of the TC layer (about 519 μ m), which is conducive to our assessment of the remaining life of the blade. For the 100 μ m surface crack, we need to use OCT as a detail supplement, the resolution of which facilitates detection down to the 10 μ m level.

4. Conclusions

The above experiments completed the detailed evaluation of the debonding defects, high-temperature oxidation cracks, and etched cracks on the TBCs by TPI and OCT systems.

- (1) A TPI system was used to detect the typical defects of the TBCs, such as debonding defects and etched cracks. It was verified that the size of debonding defects larger than 2 mm and the etched defects above 200 µm could achieve good qualitative and quantitative measurement results (100 µm defect can be hard to obtain). It was also verified that the thickness of the penetrable TC layer exceeds 500 µm. However, the detection of high-temperature oxide cracks by TPI failed because of the resolution limitation of TPI.
- (2) The typical defects of TBCs (surface etched cracks and high-temperature oxidation cracks) were evaluated by the OCT system. The results show that the hightemperature oxidation cracks can be detected by OCT with short coherence length and higher resolution, and the repeated etched circular pits of surface etched cracks can be observed better than by the TPI system. OCT can also easily measure the width and depth of etched cracks on 100 µm surfaces, with a relative error of only

5%. The high precision measurement of OCT systems complements the TPI detection information characteristics, but it can only complete the shallow surface crack measurement. This conclusion is demonstrated objectively by comparing the onedimensional time-domain signal of terahertz with the one-dimensional time-domain signal of OCT.

Overall, OCT can detect etched defects with a width as small as 100 μ m (even hightemperature oxidation cracks of about 35 μ m can be seen), and TPI can detect TC layers with a thickness of more than 500 μ m. Thus, it is concluded that the TPI method can achieve a larger detection depth, while the OCT system can improve the detection resolution at the expense of its penetration depth in the sample. When the same TBC sample is working and produces various types of defects, OCT can be used to measure the small surface defects of the sample, while TPI can measure the internal defects. The two methods can be comprehensively used in TBC defect measurement, which presents the opportunity to obtain more sample information and makes it easier to monitor and comprehensively evaluate TBC faults in a timely manner. We may evaluate more small cracks on the surface when there are also defects in deeper areas inside the sample. This will result in a higher resolution and better depth information than using UT or ECT alone (can detect the thickness of about 200 μ m of TC layer). In general, it enriches the measuring means and possibilities of TBCs. Our ongoing work is focused on investigating the fusion of TPI and OCT images of the same sample to provide more intuitive information.

Author Contributions: Conceptualization, M.L. and S.Z.; methodology, M.L. and S.Z.; software, M.L.; validation, M.L. and Y.H.; formal analysis, M.L.; investigation, M.L. and Z.Z.; resources, M.L. and Y.H.; data curation, M.L. and Z.Z.; writing—original draft preparation, M.L.; writing—review and editing, M.L., S.Z. and W.T.; project administration, M.L., S.Z. and W.T.; funding acquisition, M.L. and S.Z. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Youth Fund of the National Natural Science Foundation of China, grant number 52101355; the Youth Fund of the Fujian Provincial Natural Science Foundation, grant number 2022J05256; Fujian Provincial Natural Science Foundation, grant number 2022J01116; Fujian Province science and technology innovation key research and industrialization projects, grant number 2023XQ017; and the Open Project of Fujian Provincial Key Laboratory of Terahertz Functional Devices and Intelligent Sensing, grant number FPKLTFDIS202305.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Data are contained within the article.

Acknowledgments: We thank the East China University of Science and Technology and Beijing Institute of Technology for providing the experimental samples. We also thank Walter Nsengiyumva for his suggestions and revisions to the article.

Conflicts of Interest: The authors declare no conflicts of interest.

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Article



Optimized Tribological Performance of Nitrogen-Doped Diamond-like Carbon Films on NBR: Influence of Bias Voltage of DC Magnetron Sputtering

Tao Yang, Changxin Han, Qiaoyuan Deng and Feng Wen *

Special Glass Key Laboratory of Hainan Province, School of Materials Science and Engineering, Hainan University, Haikou 570228, China; 19080500110014@hainanu.edu.cn (T.Y.); hcx0919@hainanu.edu.cn (C.H.); qydeng@hainanu.edu.cn (Q.D.)

* Correspondence: fwen323@hainanu.edu.cn

Abstract: In this research, nitrogen-doped diamond-like carbon (N-DLC) coatings were deposited on Nitrile Butadiene Rubber (NBR) substrates using direct current magnetron sputtering (DC-MS) under varying bias voltages. This study aimed to explore environmentally friendly, low-wear, and nonlubricating seal coatings to enhance the durability of rubber sealing products, which predominantly operate under dynamic sliding conditions. By reducing the coefficient of friction (CoF), the friction and wear on rubber products can be significantly minimized, extending their lifespan. This investigation thoroughly examined the microstructure, mechanical properties, and tribological behavior of the N-DLC films. Among the coatings, the one produced at a bias voltage of -50 V demonstrated superior hardness, elastic modulus, and the lowest CoF in comparison to those prepared with 0, -100, and -200 bias voltages. This optimal combination of properties resulted in an exceptionally low wear rate of 10^{-9} for the film deposited at -50 V, indicating its outstanding wear resistance.

Keywords: NBR; DLC films; nitrogen-doped; bias voltage; tribological properties

1. Introduction

NBR, a synthetic rubber copolymer derived from butadiene and acrylonitrile, boasts high resistance to oils, fuels, and other petroleum-based substances, rendering it ideal for seals, gaskets, O-rings, and hoses in automotive and machinery applications [1]. Its exceptional sealing properties, coupled with its resistance to oils and fuels, have cemented its popularity in engines, hydraulic systems, and various machinery components [2]. However, despite its numerous merits, NBR is frequently utilized in seals and gaskets where wear resistance is paramount. Given that these components endure repeated compression and movement and are challenging to replace frequently, enhancing the service life of NBR is imperative [3,4]. Consequently, the wear resistance of NBR plays a pivotal role in ensuring an extended service life.

DLC (diamond-like carbon) films, consisting of materials exhibiting properties akin to diamond, are thin coatings valued for their hardness, wear resistance, and low friction across diverse industrial and technological realms [5-10]. Typically amorphous, DLC films comprise a blend of sp² (graphite-like) and sp³ (diamond-like) carbon bonds, endowing them with diamond-like characteristics [11]. DLC films, known for their diamond-like hardness, have excellent wear and abrasion resistance, making them ideal for durable applications. Their hardness and low CoF often lead to their use in enhancing surface wear resistance, thereby prolonging component lifespan and minimizing maintenance or replacement needs. Moreover, their chemical compatibility with rubber, owing to their shared carbon composition, coupled with their adjustable properties and diverse structures, positions them as optimal materials for fortifying the wear resistance of rubber surfaces [12].

While the surface modification of rubber with DLC films offers numerous advantages, there are also some potential drawbacks and challenges associated with this process. DLC

Citation: Yang, T.; Han, C.; Deng, Q.; Wen, F. Optimized Tribological Performance of Nitrogen-Doped Diamond-like Carbon Films on NBR: Influence of Bias Voltage of DC Magnetron Sputtering. Nanomaterials 2024, 14, 564. https://doi.org/ 10.3390/nano14070564

Academic Editors: Jose Maria De Teresa, Ricardo Lopez Anton and Sion Federico Olive Méndez

Received: 16 February 2024 Revised: 16 March 2024 Accepted: 18 March 2024 Published: 24 March 2024



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coatings present a few limitations: (1) high residual stress, (2) poor thermal stability, and (3) inevitable pinhole-like defects [13]. Elemental doping has become a notable method for addressing these issues. Nitrogen doping, in particular, has shown promise in enhancing the hardness and wear resistance of the coating. Nitrogen incorporation can alter the microstructure of the DLC film, resulting in improved mechanical properties and heightened resistance to wear and abrasion [14–16]. Additionally, as per findings from our previous study [17], nitrogen doping can augment the adhesion of the DLC coating to the NBR substrate. Enhanced adhesion is crucial for ensuring the durability and long-term performance of the coating. N-DLC coatings demonstrate potential in various practical applications owing to their robust mechanical performance and favorable tunability in terms of structure and morphological features.

Magnetron sputtering stands out as a favored technique for depositing carbon-based films owing to its versatility, precise control over film properties, and scalability [18]. Key processing parameters encompass bias voltage, temperature, working gas species, and pressure [19]. Among these factors, bias voltage holds significant sway over the energy of ions bombarding the substrate surface, thereby exerting a pivotal influence on the properties of the deposited film. This influence can be effectively harnessed to adjust adhesion and overall performance by modulating the sp²/sp³ ratio and controlling the microstructure. An elevated bias voltage typically corresponds to heightened ion energy, facilitating the nucleation and growth of crystalline phases albeit potentially introducing more defects and stress into the film [20]. An optimal sp³C fraction, particularly for hydrogen-free DLC coatings, is attainable within a bias voltage range of 100–200 V [21]. Similarly, a-C:H coatings characterized by high hardness and adhesion can be achieved through a meticulous control of bias voltage in radio frequency-based plasma-enhanced chemical vapor deposition (PECVD) [22]. Notably, bias voltage does not exert a distinct influence on the nitrogen content of films [23]. However, nitrogen doping prompts alterations in the sp^2C/sp^3C ratio and surface C/O ratios [24]. These variations in bond fractions significantly impact the hardness, CoF, and wear resistance of DLC coatings.

In the present investigation, N-DLC films were deposited directly onto NBR substrates using DC-MS. This study comprehensively examined the impact of varying bias voltages during the film deposition process on the surface morphology, structural characteristics, wettability, mechanical attributes, and tribological performance of N-DLC films. Additionally, the investigation succinctly elucidated the frictional interaction mechanisms of N-DLC films against rubber materials. The findings provide novel insights into the enhancement of rubber seal surfaces through modification techniques.

2. Materials and Methods

2.1. Deposition of N-DLC Films

The N-DLC coatings were applied to NBR substrates via reactive magnetron sputtering within an atmosphere composed of argon and nitrogen gases. Prior to the coating process, the rubber substrates were subjected to a meticulous cleaning regimen. This commenced with the application of a detergent solution, followed by submersion in boiling water for a duration of three minutes. The subsequent phase involved ultrasonic cleansing in anhydrous ethanol for ten minutes, this process was repeated in cycles until the ethanol solvent remained colorless post cleansing, indicating the removal of impurities such as dirt and wax. These preparatory steps were crucial for enhancing the adhesion between the deposited film and the rubber substrate [25]. To conclude the cleaning process, the rubber samples were dried using a hairdryer set to blow cold air, preparing them for the deposition of the N-DLC films.

The schematic representation of the apparatus utilized for the synthesis of N-DLC films via magnetron sputtering is depicted in Figure 1. This setup comprises a high-purity graphite target (φ 76.2 mm × 4 mm, 99.99% purity) positioned within a sputtering chamber that achieves a base vacuum of 3.0×10^{-3} Pa. The sputtering process was powered at 100 W, employing a frequency of 40 kHz with a 75% duty cycle. Argon gas was introduced

at a flow rate of 30 sccm to serve as the sputtering medium, while nitrogen gas was fed at a rate of 3 sccm to incorporate nitrogen into the DLC films. The substrate bias voltage was varied across four levels: 0 V, -50 V, -100 V, and -200 V, facilitating the deposition of a series of N-DLC films, designated as V0, V50, V100, and V200, onto NBR surfaces and silicon wafers over a 60 min duration. Prior to film deposition, a two-step pre-treatment involving argon plasma was conducted to ensure optimal film adhesion by removing oxides and impurities from the rubber and target surfaces, respectively. The first step was to clean the rubber surface with 30 sccm argon gas at 3.0 Pa, -600 V bias voltage, 75% duty cycle, and 40 kHz. This process lasted for 15 min. The second step was to clean the carbon target at 1.4 Pa, argon flow rate of 30 sccm, 75% duty cycle, 40 kHz, and 100 W DC power. This process lasted for 10 min. This comprehensive setup and procedural detail are summarized in Table 1, illustrating the meticulous approach to N-DLC film preparation via magnetron sputtering.



Figure 1. Schematic of the equipment for the preparation of N-DLC films via magnetron sputtering.

Table 1. Process parameters for N-DLC film preparation under different bias voltages.

		Flow Rate (sccm)					
No.	Bias Voltage (V)	Press (Pa)	Power (W)	Ar	N_2	Time (min)	Temperature (°C)
V0	0	1.4	100	30	3	60	25
V50	-50						
V100	-100						
V200	-200						

2.2. Material Characterization

The surface morphologies of the samples were examined utilizing an atomic force microscope (AFM, Nanosurf AG Co., Liestal, Switzerland) in tap mode with a silicon probe (Tap 190Al-G, Nasser (Shanghai) Nanotechnology Co., Ltd., Shanghai, China) across a scan area of 10 μ m × 10 μ m. For visualizing both the surface and cross-sectional morphologies of the films, as well as the surface morphology of the samples' test area, post-tribological and bonding assessments and a scanning electron microscope (SEM, Quanta 250, Thermo Fisher Scientific Co., Waltham, MA, USA) were employed. The chemical bonding structure and composition of the DLC films were analyzed through Raman spectroscopy (inVia Reflex, Renishaw Co., New Mills, UK, with a laser wavelength of 514.5 nm) and X-ray photoelectron spectroscopy (XPS, Escalab Xi+, Thermo Fisher Scientific, Waltham Co., MA, USA). Notably, the analysis chamber for the XPS was maintained at a vacuum level of 8×10^{-10} Pa, utilizing Al k α -rays (hv = 1486.6 eV) as the excitation source.

The contact angle (CA) measurements were conducted at ambient temperature using a JC2000 contact angle tester, employing the sessile drop method. To minimize the influence of the droplet's own weight, it was crucial to maintain a small droplet volume, which was controlled at 1 μ L. For the assessment of all materials, two liquids were chosen: the non-polar CH₂I₂ and polar H₂O. The CA values were recorded 15 s subsequent to the droplet deposition. The solid surface energy (γ s), along with its polar (γ ^P_S) and dispersion (γ ^S_S) components of surface energy, were calculated utilizing the Owens–Wendt–Rabel–Kaelble (OWRK) method [26]. For each combination of liquid and surface, measurements were repeated three times to reduce uncertainty.

A Berkovich diamond indenter was utilized for conducting nanoindentation experiments (CETR-UMT, Bruker Co., Karlsruhe, Germany). The applied load was incrementally increased from 0 to a peak load of 1 mN over a duration of 15 s, followed by a creep phase lasting 10 s, and a subsequent unloading phase of 15 s. To account for thermal drift, the procedure included a 45 s stabilization period when the load was reduced to 0.1 mN. To mitigate the influence of residual stress from adjacent indentations, five indentations were executed on each sample across five distinct positional zones, maintaining a separation of 20 μ m between successive indentation points.

A diamond-tipped scratch tester with a stylus cone tip curvature radius of 12.5 μ m was utilized to assess the adhesion strength of the N-DLC coatings quantitatively. The stylus traversed the coatings with a load incrementally increasing from 10 mN to 600 mN over 100 s, at a constant velocity of 20 μ m/s. The critical load, marked by an abrupt frictional change, was recorded to gauge the coatings' adhesive force. For tribological analysis, a CETR-UMT ball-on-disk apparatus from Bruker was employed at room temperature. Zirconia balls with a 3 mm radius were used against the samples, with a corresponding track radius of 6 mm, at 100 rpm and a 0.3 N load for a 60 min test duration. The above test procedure was repeated at least three times to ensure the reliability of the experiment.

$$K = V/(F \times L) \tag{1}$$

In the context of material wear, the rate of wear, denoted as K, is determined by the ratio of the volume of material worn away, represented by V, to the product of the applied load, F, and the total distance traversed by the moving contact, symbolized by L. The calculation of the wear volume V is as follows:

$$Y = A \times d$$
 (2)

The wear track's cross-sectional area, denoted as *A*, situated beneath the specimen surface's horizontal line, was quantified using a 3D optical profiler (UP-Lambda, Rtec Co., San Jose, CA, USA). The variable *d* represents the wear track's length.

V

3. Results and Discussion

3.1. Morphology

To investigate the surface morphology of the film, the authors employed SEM to characterize N-DLC films prepared under varying bias voltages, ranging from low to high, as depicted in Figure 2. In observing the surface morphology of the rubber, it can be found that the rubber injection molding process leaves some perforations and protrusions on the surface of uncoated NBR, which are clearly visible in Figure 2b. The findings indicate that the surface of V50 is notably uniform, exhibiting minimal undulations and stratification, with only a sparse presence of particles. However, with increasing bias voltage, particle agglomeration occurs on the surfaces of films V100 and V200. This phenomenon is likely attributed to the heightened injection energy resulting from the increased bias voltage, leading to the agglomeration of atoms and molecules in the vacuum chamber. Ionized ions, with a smaller mean free path, facilitate sediment agglomeration. Conversely, the film prepared at 0 V displayed a rough morphology due to the absence of negative bias attraction from the substrate. Consequently, it becomes challenging for C and N elements

within the cavity to accumulate on the surface of a non-conductive matrix, such as NBR, preventing them from filling the rubber and resulting in defects and voids on the rough surfaces. In contrast, the N-DLC film prepared at -50 V exhibited a relatively smoother surface morphology, attributed to the beneficial effects of an appropriate negative bias. Under the regulation of -50 V, ionized plasma could refine the rough surface of the NBR matrix derived from rolling and stamping [27]. The thicknesses of these sedimentary thin films ranged from about 150 to 180 nm.



Figure 2. Surface morphologies of NBR and N-DLC films prepared on NBR using different substrate bias voltages. NBR: (**a**–**d**); V00: (**e**–**h**); V50: (**i**–**l**); V100: (**m**–**p**); V200: (**q**–**t**).

In addition, the authors performed macroscopic measurements of the morphology density and roughness of each N-DLC film on NBR as well as on the rubber surface (2 mm \times 1.5 mm), as shown in Figure 2c,g,k,o,s. It is worth noting that there is a significant difference between the initial NBR surface and the coated NBR surface. The roughness properties of the surfaces of the film-coated samples were all reduced to varying degrees, with the V50 film having the smallest roughness of 6.96 µm. In contrast, the roughness of V0 was relatively large at 12.6 µm, which is almost comparable to the roughness observed in the V200 samples, which was about 13.0 µm. However, at the macroscopic level, the surface roughness was more affected by the characteristics of the substrate. Given the inherent high roughness of NBR, the roughness of the films may be affected by the substrate and exhibit a corresponding roughness.

In order to investigate the roughness properties of the films in depth, we used atomic force microscopy (AFM) to characterize the micromorphology of each sample, as shown in Figure 2d,h,l,p,t. The surface roughness of V50 remains the lowest at 69.51 nm, while V100 and V200 continue to show higher roughness values and agglomeration. The films prefabricated at 0 V show an inhomogeneous shape and their three-dimensional morphology retains the rift valley configuration, which indicates that the plasma dispersion failed to fill the debris defects in the NBR.

3.2. Structure and Composition

For single-crystal graphite, a singular Raman peak emerged near 1580 cm⁻¹, attributed to the central vibration mode within the optically allowed E2g region of crystallized graphite. This peak, denoted as the G peak [28,29], signifies the presence of sp² C-C hybrid bonds. Conversely, diamond is characterized by a distinct Raman peak at 1322 cm^{-1} , which originates from the T_{2g} symmetric vibration mode, signifying the presence of sp³ C-C hybrid bonds. The disruption of long-range order leads to the emergence of a peak around 1360 cm⁻¹, known as the D peak, which is attributed to phonon dissipation at the boundary of the Brillouin zone [30-32]. The emergence of the D peak is indicative of disorder within the sp² hybridized bond angles, suggesting the presence of sp² hybridized carbon structures composed of graphite rings. In all samples depicted in Figure 3, distinct peaks are observable, alongside an additional peak near 1415 cm^{-1} , which can be attributed to aromatic substituents in the NBR [4]. During the sputtering process, the temperature within the vacuum chamber was initially at 25 $^\circ$ C ambient temperature and did not exceed 120 $^\circ$ C at the end of deposition process. This temperature is substantially below the degradation temperature of NBR, which is 295 °C [33]. Carbon plasma bombardment on the surface of NBR can induce the random scission of polymer chains, leading to the formation of reactive groups. These groups may undergo internal reactions, migrate to the surface, or engage in reactions with carbon atoms, resulting in the formation of complex cross-linked structures. Additionally, carbon atoms may interact with unpaired sp² bonds present in NBR, facilitating the formation of six-membered rings, thereby reducing the internal energy of the system [34,35]. Typically, the Raman spectrum of a DLC film is characterized by an asymmetric broad peak located near 1500 cm⁻¹ [10].



Figure 3. (a) Peak fitting of the Raman curves of each sample under different bias voltages to obtain the Raman curves of each sample and their respective I_D/I_G values; (b) G peak position and FWHM of each sample; (c) peak area fraction of each sub-peak obtained through Gaussian peak fitting.

In order to obtain more precise information about the carbon bonding structure in the N-DLC film on NBR, a Gaussian fit was applied to the Raman spectra with baseline subtraction followed by back-convolution, and a sub-peak fit with three peaks is shown in Figure 3a. The qualitative estimation of the sp³ hybridization ratio was achieved by calculating the I_D/I_G value from the areas under the D peak and G peak [36]. Generally, an increase in sp³ hybrid bonds correlates with a decrease in the I_D/I_G ratio. As illustrated

in Figure 3a, with the bias voltage rising from 0 V to -200 V, the I_D/I_G initially decreases and then gradually increases. Alongside the subsurface injection model, low C⁺ incident energy leads to energy consumption through collective atom collisions, hindering the penetration of atoms onto the coating surface. Within a certain range of energy increase, C^+ penetrates the surface, becoming interstitial atoms in the subsurface layer, thereby increasing local density and compressive stress. The application of compressive stress encourages the atomic groups within diamond-like carbon (DLC) to transition into a stable phase characterized by sp² hybrid bonds. As illustrated in Figure 3b, there is a depiction of the variations in the G peak's position and its full width at half maximum (FWHM) as a function of the applied bias voltage. An initial increase in bias voltage leads to a broadening followed by a narrowing of the G peak's half-peak width. Conversely, the peak's position undergoes the opposite trend. This observation underscores the advantageous impact of elevated bias voltage on the formation of sp² bonds within the nitrogen-doped DLC (N-DLC) film. Such an effect is likely attributable to the high bias voltage facilitating the substitution of carbon atoms with nitrogen within the sp³ bond structure, which in turn diminishes the average coordination number from four to three. Furthermore, the higher electronegativity of nitrogen atoms (3.0) in comparison to carbon atoms (2.5) results in an electron cloud distribution that is skewed toward nitrogen atoms. This skewing weakens the carbon-carbon bond and modifies the coordination number from four. This alteration has implications for the stability of the sp³ structure and, by extension, influences the hardness of the film [37].

A Gaussian peak fitting analysis revealed the area proportion of each subpeak in Figure 3c. In particular, sample V0 shows a higher proportion of aromatic substituents, potentially due to the rough surface and uneven coverage of the DLC film, making it susceptible to the Raman excitation wavelength of 514.5 nm [38].

Moreover, the proportions of sp² and sp³ configurations were determined through X-ray photoelectron spectroscopy (XPS) analysis. Figure 4 distinctly displays the significant asymmetry observed in the C 1s spectral line. The integration of nitrogen atoms into the carbon matrix, resulting in the formation of C-N bonds, leads to a shift of the peak position toward higher binding energies. The XPS analysis indicates that nitrogen doping leads to an upshift in the C 1s peak binding energies, attributed to nitrogen's higher electronegativity compared to carbon. This results in an electron density shift toward nitrogen in the C-N covalent bond. Moreover, the binding energy of the C-N bond, encompassing both sp²C-N and sp³C-N configurations and is found to be higher than that of the C-C bond, including sp²C-C and sp³C-C structures. In drawing from the literature [37], the binding energies for the five distinct peak positions are identified as follows: 284.6 eV for the sp²C-C bond, 285.2 ± 0.1 eV for the sp³C-C bond, 286.1 ± 0.1 eV for the sp²C-N bond, 287.4 ± 0.2 eV for the sp³C-N bond, and 291.5 ± 0.1 eV for the C-O bond. Additionally, the sp³ bond concentration initially increases and then decreases with rising substrate bias, aligning with the I_D/I_G ratio trend observed in the Raman spectroscopy.

The initial N 1s spectrum underwent deconvolution, revealing two prominent peaks with binding energies of 398.6 ± 0.1 eV and 399.8 ± 0.2 eV, respectively [39]. The peak at the lower binding energy is attributed to the sp³ hybridized C-N bond, while the peak at the higher binding energy corresponds to the sp² hybridized C-N bond. As depicted in Figure 5, the ratio of sp² C-N to sp³ C-N initially decreases and then increases with the escalation of substrate bias. This trend indicates that the formation of sp² C-N structures becomes more favorable as the bias voltage increases. This phenomenon can be explained by the differing chemical stabilities between the sp² C-N and sp³ C-N bonds.



Figure 4. (a-d) C 1s XPS fine spectrum of as-prepared N-DLC coating.



Figure 5. (a-d) N 1s XPS fine spectrum of as-prepared N-DLC coating.

3.3. Contact Angle and Surface Energy

Figure 6a displays a photograph of the water contact angle (CA) of the V50 sample, indicating a measurement of 117.75 degrees, which is indicative of significant hydrophobicity. Figure 6b depicts the CA change curve in the presence of water and diiodomethane, demonstrating distinct surface wettability characteristics of N-DLC films fabricated under various substrate biases. Notably, both the NBR matrix and the N-DLC film coated on NBR exhibit CA values exceeding 90° when in contact with water, suggesting hydrophobic properties. The curve shows a slight increase in CA with increasing negative substrate bias, peaking at 117 degrees at -50 V. Subsequently, with further negative substrate bias intensification, the water CA begins to decrease but consistently remains higher than that of NBR. Surface roughness generally correlates negatively with CA values, which is consistent with prior roughness observations.



Figure 6. (a) Contact angle of V50-H₂O; (b) water contact angle and diiodomethane contact angle of each sample; (c) surface energy of each sample.

In Figure 6c, the OWRK method was employed to calculate the total surface energy and its polar and dispersion components for both the NBR substrate and the N-DLC film. The surface energy of NBR primarily consists of a single dispersed component. A clear influence of substrate bias on surface energy is evident across all samples. Upon N-DLC film deposition, the total surface energy initially decreases and then increases with rising bias voltage, reaching a minimum of about 7.18 mJ/m² at -50 V. Furthermore, as the bias voltage continues to increase, the surface energy notably rises, which is consistent with previous findings on surface roughness. In all examined samples, including the NBR substrate, the dispersion component (γ_{s}^{c}) of the surface energy was notably high, often matching or surpassing the total surface energy ($\gamma_{\rm S}$), with the exception of sample V50, which displayed the lowest surface energy. Notably, the polar component (γ_{S}^{p}) of surface energy remained minimal across all samples, highlighting that variations in the surface energy of DLC films deposited on NBR are predominantly attributed to the dispersive components rather than the polar components or the total surface energy. This indicates that the dispersion component plays a pivotal role in determining the interfacial wetting behavior of the N-DLC film, particularly in terms of wettability and solid–liquid interactions.

3.4. Mechanical Properties

Figure 7a presents a distinct load-depth indentation profile for each sample. The indenter's penetration into the specimen's surface during the loading stage induces simultaneous elastic and plastic deformation. The subsequent unloading phase allows for elastic recovery, enabling the determination of both the hardness and elastic modulus. Figure 6b,c show the changes in hardness and Young's modulus for NBR and N-DLC films on NBR substrates under varying bias voltages. Typically, hardness correlates with the area affected by the maximum indentation depth (h_{max}), while Young's modulus is linked to the observed changes in hardness [6]. After unloading, the indentation rebounds much deeper than the thickness of the DLC (about 180 nm). Thus, the hardness value represents the composite hardness of the film and substrate, calculated using the Oliver-Pharr method [27]. Initially, the film's hardness and Young's modulus increase and then decrease with increasing substrate bias. A peak hardness of 6.8 MPa was observed at a bias of -50 V. This may be attributed to the decline in the sp³ content of the film as the bias voltage increases, signifying more graphite bonds and fewer diamond-like bonds, thereby reducing the film's hardness and elastic modulus. A higher substrate bias (>-150 V) also induces the formation of soft second phases in N-DLC, characterized by highly graphitized or nitrogen-rich carbon regions. These second phases diminish the mechanical properties and stability of the film. The values of H/E and H^3/E^2 , depicted in Figure 7d,e, serve as indicators of the film's resistance to crack formation and plastic deformation, respectively. These metrics are positively associated with the film's wear resistance, suggesting that higher values denote enhanced durability [40,41]. With increasing bias voltage, the H/E and H^3/E^2 values initially increase before decreasing. This phenomenon is attributed to the suitable bias voltage facilitating a smooth transition between NBR and N-DLC, providing the V50 film with notable toughness and strong resistance to plastic deformation, thereby reducing the risk of brittle fracture.



Figure 7. (a) Load–unloading curve of each sample; (b) hardness of each sample; (c) Young's modulus of each sample; (d) H/E of each sample; (e) H^3/E^2 of each sample; (f) adhesion strength of each sample.

3.5. Tribological Properties

To evaluate the tribological properties of N-DLC films, rotational friction tests were conducted on NBR-coated N-DLC samples across varying bias voltages, with the results depicted in Figure 8. In Figure 8a,b, the evolving trend of the CoF curve for each sample over time and its average CoF during the friction process are presented. It is apparent that despite displaying differing CoF values, all samples under varied bias voltages exhibit a significant reduction compared to the NBR matrix. The NBR rubber not only displays an average CoF as high as 2.2, but also demonstrates substantial fluctuations during the friction process, indicating poor wear resistance. Conversely, the modified N-DLC film markedly reduces the CoF, notably the V50 sample, boasting an average CoF as low as 0.05, highlighting its wear resistance. Moreover, as inferred from the wear rate (depicted in Figure 8c), compared to NBR, the wear rate was reduced by two orders of magnitude. Consequently, the V50 sample not only demonstrates good wear resistance, but also exhibits excellent durability.

The wear scar morphology of each sample, as illustrated in Figure 8d–r, reveals minimal wear for specimens V50 and V100. An adhesion strength analysis indicated that sample V50 exhibited the highest bonding strength, with a coefficient of friction (CoF) around 0.05, and the lowest wear rate, measured at 10^{-9} . A three-dimensional wear trace analysis showed minor wear with visible debris for samples V0 and V200, as confirmed via SEM testing. In contrast, V50 and V100 displayed exceptional wear resistance, with no visible wear marks, aligning with the three-dimensional wear trace representation. The wear area on the V50's surface was barely noticeable, featuring only occasional protrusions, likely surface impurities. In addition, a small number of bumps are vaguely visible beyond the wear marks in the three-dimensional wear trace diagram (pointed out by the white arrows in the diagram), which are attributed to impurity particles in the rubber substrate itself. Therefore, applying a moderate substrate bias can significantly improve the N-DLC film's adhesion to the substrate, enhancing wear resistance under low-friction conditions and ensuring durability under continuous wear.



Figure 8. (a) Coefficient of friction of each sample; (b) average coefficient of friction of each sample; (c) wear rate of each sample. Wear depth cross-section and 3D wear trajectory morphology of N-DLC films on NBR with different bias voltages, NBR: (d–f); V0: (g–i); V50: (j–l); V100: (m–o); V200: (p–r).

Additionally, to examine the structural alterations at the wear scars, Raman spectroscopy was performed on these regions. Figure 9a depicts the fitting outcomes of the Raman spectra for each sample. Furthermore, an investigation into the peak position and FWHM of the Raman G peak at the wear scars was conducted. At a wear scar, the G peak position deviates to varying degrees from the standard G peak at 1580 cm⁻¹, with a greater offset indicating higher internal stress [42]. The V50 sample still exhibited minimal internal stress, attributed to the effective combination of N-DLC prepared under a -50 V bias and NBR. Figure 9d illustrates the I_D/I_G ratio for each sample before and after the friction test. A noticeable increase in the I_D/I_G ratio is observed for all samples, suggesting that the samples experienced heating during the friction process, leading to distinct alterations [43]. With increasing graphitization, the graphite wear debris acts as a transfer layer and solid lubricant, resulting in a significant reduction in the CoF.

The mechanical properties of the film samples prepared under different bias pressures were compared, and comparison results were plotted in Figure 10. As illustrated in Figure 10, the mechanical properties of the V50 sample exceled in all aspects compared to those of other samples within the same group. It is noteworthy that the wear resistance index is derived by reciprocating the CoF.



Figure 9. (a) Raman spectra of the wear marks of each sample; (b) G peak position of each sample; (c) FWHM of each sample; (d) I_D/I_G ratio of each sample before and after the friction test.



Figure 10. Comparison of mechanical properties between samples.

4. Mechanism Discussion

Figure 11 illustrates the N-DLC friction reduction mechanism and the impact of high bias voltage on N-DLC film performance, alongside experimental findings. Figure 11a,b depict the tribological mechanism of N-DLC in an air environment. Consistent with the Raman results at the wear marks, a consistent upward trend in the I_D/I_G is observed after all samples undergo 1 h of rotational friction. This indicates the potential graphitization of N-DLC due to heat during friction, leading to the formation of a soft transfer film that improves rubber–film friction properties. Additionally, Figure 11c shows that a high bias voltage (>150 V) during magnetron sputtering readily induces the formation of a soft second phase on the film surface, represented as the (CN)x phase, in Figure 11b,d, and graphite phase [44]. This soft second phase contributes to N-DLC films under high bias voltages exhibiting a higher I_D/I_G ratio and lower hardness, thereby reducing their tribological properties [45]. Consequently, in the preparation of N-DLC films, selecting



an appropriate and moderate bias voltage is crucial for enhancing both mechanical and tribological properties.

Figure 11. (*a*,*b*) Friction reduction mechanism of N-DLC film in air; (*c*,*d*) effect of high bias voltage on N-DLC film.

5. Conclusions

In this investigation, the DC magnetron sputtering (DC-MS) method was utilized to coat NBR with N-DLC films, aiming to improve its tribological characteristics. The study assessed how varying bias voltages influenced the N-DLC films' surface morphology, structural composition, wettability, and tribological performance. The following insights were derived from the research findings:

- (1) The substrate bias voltage plays a pivotal role in determining the surface morphology, structural composition, and surface roughness of N-DLC films produced through DC-MS technology, thereby affecting their wettability, mechanical properties, and tribological performance. An increase in bias voltage results in the incorporation of softer second phases, such as (CN)x and graphite, into the N-DLC film. These softer constituents adversely impact the film's mechanical and tribological properties.
- (2) Moderate bias application was found to enhance the bonding strength between DLC and rubber, along with their tribological performances. At a bias of -50 V, N-DLC films exhibited commendable adhesion to the substrate and tribological characteristics. The coefficient of friction (CoF) remained consistently low at 0.052 throughout the friction testing, and the film showed no significant wear marks post experiment. However, the adhesion of NBR coated with N-DLC film was compromised under relatively high bias conditions during the deposition process.
- (3) N-DLC films applied to NBR surfaces demonstrate enhanced tribological characteristics primarily due to increased hardness, improved adhesion between the film and substrate, reduced surface roughness, and diminished adhesion at the friction interface.

Author Contributions: Data curation, T.Y. and C.H.; funding acquisition, Q.D. and F.W.; investigation, T.Y.; project administration, Q.D. and F.W.; writing—original draft, T.Y. and C.H.; writing—review and editing, T.Y. and F.W. All authors have read and agreed to the published version of the manuscript.

Funding: This project was supported by the Hainan Provincial Natural Science Foundation of China (420RC525, 520QN225) and Hainan Province Science and Technology Special Fund (ZDYF2019206).

Data Availability Statement: The data presented in this study are available from the corresponding author upon request.

Acknowledgments: The authors thank the assistance provided by Hainan University Analysis and Testing Center.

Conflicts of Interest: The authors declare no conflicts of interest.

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Article Monolithic Use of Inert Gas for Highly Transparent and Conductive Indium Tin Oxide Thin Films

Hessa I. Alabdan^{1,2}, Fahad M. Alsahli^{1,3}, Shubhranshu Bhandari¹ and Tapas Mallick^{1,*}

- ¹ Environment and Sustainability Institute, University of Exeter, Penryn Campus, Cornwall TR10 9FE, UK; hima201@exeter.ac.uk (H.I.A.); fa419@exeter.ac.uk (F.M.A.); s.bhandari@exeter.ac.uk (S.B.)
- ² Department of Physics and Renewable Energy, College of Science and Humanities-Jubail, Imam Abdulrahman Bin Faisal University, Jubail 35811, Saudi Arabia
- ³ Physics Department, University of Hafr Al Batin, Al Jamiah, Hafar Al Batin 39524, Saudi Arabia

* Correspondence: t.k.mallick@exeter.ac.uk; Tel.: +44-(0)-1326-259465

Abstract: Due to its excellent electrical conductivity, high transparency in the visible spectrum, and exceptional chemical stability, indium tin oxide (ITO) has become a crucial material in the fields of optoelectronics and nanotechnology. This article provides a thorough analysis of growing ITO thin films with various thicknesses to study the impact of thickness on their electrical, optical, and physical properties for solar-cell applications. ITO was prepared through radio frequency (RF) magnetron sputtering using argon gas with no alteration in temperature or changes in substrate heating, followed with annealing in a tube furnace under inert conditions. An investigation of the influence of thickness on the optical, electrical, and physical properties of the films was conducted. We found that the best thickness for ITO thin films was 100 nm in terms of optical, electrical, and physical properties. To gain full comprehension of the impact on electrical properties, the different samples were characterized using a four-point probe and, interestingly, we found a high conductivity in the range of $1.8-2 \times 10^6$ S/m, good resistivity that did not exceed $1-2 \times 10^{-6}$ Ω m, and a sheet resistance lower than 16 Ω sq⁻¹. The transparency values found using a spectrophotometer reached values beyond 85%, which indicates the high purity of the thin films. Atomic force microscopy indicated a smooth morphology with low roughness values for the films, indicating an adequate transitioning of the charges on the surface. Scanning electron microscopy was used to study the actual thicknesses and the morphology, through which we found no cracks or fractures, which implied excellent deposition and annealing. The X-ray diffraction microscopy results showed a high purity of the crystals, as the peaks (222), (400), (440), and (622) of the crystallographic plane reflections were dominant, which confirmed the existence of the faced-center cubic lattice of ITO. This work allowed us to design a method for producing excellent ITO thin films for solar-cell applications.

Keywords: indium tin oxide; thin films; RF magnetron sputtering; third generation solar cells

1. Introduction

Transparent conducting oxide (TCO) materials are widely used to transmit light through materials and conduct electricity. To produce these materials, metal oxides are used, which include tin oxide (SnO₂), aluminum oxide (Al₂O₃), indium oxide (In₂O₃) [1], and zinc oxide (ZnO) [2,3]. There are many uses and applications of TCOs, such as display devices like flat-panel screens and touchscreens [4]; smart windows, in which the transparency can be controlled through applying a voltage and, hence, the heat and light transmitted through the window can be controlled [5]; and optoelectronic devices such as light-emitting diodes (LEDs) and photodetectors [6]. ITO films are of crucial importance in optoelectronic devices and solar cells. ITO is mainly used as the front electrode in photovoltaic applications [7] due to its high conductivity and transparency ranges, which make it a favorable choice for fabrication. Several studies have investigated the different properties of ITO and how they can be optimized using different growth techniques and

Citation: Alabdan, H.I.; Alsahli, F.M.; Bhandari, S.; Mallick, T. Monolithic Use of Inert Gas for Highly Transparent and Conductive Indium Tin Oxide Thin Films. *Nanomaterials* 2024, *14*, 565. https://doi.org/ 10.3390/nano14070565

Academic Editors: Jose Maria De Teresa, Ricardo Lopez Anton, Alexander Tselev and Sion Federico Olive Méndez

Received: 12 February 2024 Revised: 17 March 2024 Accepted: 20 March 2024 Published: 24 March 2024



Copyright: © 2024 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). conditions. In particular, in third-generation solar cells like perovskites and dye-sensitized solar cells, several attempts have been made to increase the efficiency of lab-built ITO to be used as a front electrode through different approaches. Although ITO has many optical, electrical, and physical advantages in the field of optoelectronic devices and photovoltaics, the high manufacturing costs and scarcity of indium and tin supplies hinder the long-term viability and scalability of its usage in third-generation solar cells.

The growth technique can contribute to material savings through reducing the amount of wasted material during the synthesis process. Radio frequency (RF) magnetron sputtering is a favored method for the growth of ITO films, as it provides high uniformity and precision when it comes to the microstructure growth and the ratios of indium and tin, which can be accurately specified for the sputtering targets. Unlike liquid and chemical approaches to creating ITO, which create a large amount of wasted materials, RF magnetron sputtering can create thousands of highly transparent and uniform thin films using one sputtering target. Many studies have focused on the creation of ITO thin films with RF magnetron sputtering. In a study by Vinh Ai Dao et al. [8], they heated the substrates in the deposition process and used an oxygen flow. Their results showed proper ITO parameters and, when they used a temperature of 200 °C, the heterojunction silicon solar-cell efficiency reached 16%. In another study by M.G. Sousa et al. [9], they compared their created ITO glass with and without the use of hydrogen pressure within the chamber and with only argon but an RF power of 250 W. This also resulted in adequate properties for the ITO to be used in solar-cell applications. In a study by F. Kurdesau et al. [10], they used oxygen in the chamber alongside argon. Another recent study by Amalraj P. A et al. [11] investigated the effects of the film thickness and RF power on the optical and electrical properties of ITO films. Shumin Y. et al. [12] prepared four different ITO targets in their lab with different crystallinities and studied the effects of the crystallinity of ITO targets on the properties of the ITO films. In the study of D. Kudryashov et al. [13], they found that, with argon gas, the best power at room temperature was only 50 W, and they tested a thickness of 100 nm with different parameters that resulted in the appropriate parameters for solar-cell applications. A study published after 2020 mostly tackled ITO growth within other layers (e.g., Cu) in RF magnetron sputtering [14]. Recent published studies focused on variations in power and growth temperature, using different gases or only argon gas (the latter was quite rarely used). For this reason, we studied indium tin oxide films grown using the radio frequency magnetron sputtering technique with varying thicknesses, in order to study the effect of thickness on the film's properties using argon gas alone. Our approach had interesting results which contribute to the existing scientific literature.

2. Materials and Methods

2.1. Preparation of ITO Samples Using PVD

In this study, we used PVD (MiniLab ST060M R&D Magnetron Sputtering and Thermal Evaporation System, Moorfield Nanotechnology Limited. Cheshire, United Kingdom.) with load lock in the Environment and Sustainability Institute (ESI) solar lab to create films with different thicknesses using radio frequency sputtering. The ITO target was bought from Kurt J. Lesker, Sussex, United Kingdom, and had an indium to tin oxide ratio of $90/10 \text{ wt}\% \text{ In}_2\text{O}_3/\text{SnO}_2$. The argon gas that was pumped to the chamber was of 99.99% purity and the silica low-iron glass substrates with a 4 mm thickness and 2 imes 2 cm dimensions were obtained from Cornwall Glass Manufacturing, Plymouth, United Kingdom. The PVD was only run on the radio frequency magnetron sputtering system. The substrates were cleaned with acetone for 30 min, IPA for 30 min, and then deionized water for 30 min, all in an ultrasonic bath, and then dried in ambient air. The evacuation pressure of the chamber was less than 4×10^{-3} mbar. The ITO layers were manufactured in the radio frequency magnetron sputtering system chamber with a pressure set point of 5×10^{-3} mbar. The ITO sputtering during deposition was performed with an RF power of 70 W. The rotation speed for the substrate holder base was 20 a.u. and the Ar flow was 20 sccm. There was no increase in temperature on the base while growing the ITO films. Films with different
thicknesses were grown: 50 nm, 100 nm, 150 nm, 200 nm, 250 nm, and 300 nm. As soon as the samples were manufactured, the samples were annealed at 500 °C for 2 h, with the temperature increasing at a rate of 5 °C per minute, in a tube furnace with a nitrogen gas flow (30 L/min) and they were left inside the furnace to cool to room temperature for another 2 h. Figure 1 illustrates the fabrication process with the different parameters used to grow the samples.



Figure 1. The fabrication process of ITO samples.

2.2. Characterization Techniques

A four-point probe was used to study the films' electrical properties, as our main purpose was to find the thickness that resulted in the best electrical characteristics to be used as a front electrode. After choosing the best thickness in the context of optimal electrical properties, the optical characterization of the samples before and after annealing was performed through measuring the spectral dependence of the transmission (T(k)) of deposited ITO layers within the visible wavelength range (300–800 nm) using a spectrophotometer; through this, we calculated the absorbance and found the bandgap. Moreover, the samples' physical properties were examined using X-ray diffraction (XRD) (Bruker D8 advanced XRD, Bruker, Billerica, MA, USA); atomic force microscopy (AFM) (Bruker Innova AFM, Bruker, Billerica, MA, USA), after staining the samples with a thin carbon layer; and later, scanning electron microscopy (SEM) (Tescan Vega 3, Tescan, Brno, Kohoutovice Czech Republic). We have included the before and after annealing measurements in order to understand the influence of annealing on the optical and electrical properties.

3. Results and Discussion

3.1. X-ray Diffraction Microscopy Measurements

Figure 2 shows the X-ray diffraction microscopy results for the films with different thicknesses before annealing. Almost all identifiable peaks lost some of their intensity, indicating that the ITO films had only a minimal amount of crystallinity before the annealing process. They had an amorphous quality for the most part. However, as the layer thickness increased, crystalline characteristics started to become more apparent.

Following annealing, the X-ray diffraction patterns (Figure 3) were characterized by prominent peaks that unmistakably signified an increase in crystallinity. Because charge carriers are given organized paths within the lattice structure of ITO, facilitating charge mobility, this phenomenon has implications for improving conductivity. The (222), (400), (440), and (622) peaks are the prominent peaks for the faced-center cubic lattice of ITO crystallographic plane reflections [15–17]. The other peaks ((211), (411), (431), (521), (611), (444), and (800)) represent other planes' reflections. As the thickness increased, the preferential crystal orientation changed to the (400) plane, as the grain strain increased towards this plane due to interstitial oxygen and indium vacancies.



Figure 2. X-ray diffraction patterns of ITO films with different thicknesses before annealing.



Figure 3. X-ray diffraction patterns of ITO films with different thicknesses after annealing.

The formation of strain results from both external elements like dislocations and extended defects within the crystalline lattice, as well as intrinsic point defects like vacancies and site disorder. The calculated lattice constants showed a notable agreement with known reference values (JCPDS card No. 71-2194) [18–20].

3.2. Atomic Force Microscopy

Atomic force microscopy (AFM) measurements were used to gain an understanding of the surface morphology of the indium tin oxide (ITO) films. The experiment aimed to gain a thorough understanding of the complex interactions between the films' electrical characteristics and their underlying physical characteristics. The goal was to identify the relationship between the surface morphology and the distinctive qualities of the ITO films. Figure 4 shows a variety of unique samples of ITO films with different thicknesses. The images all have dimensions of 10 μ m \times 10 μ m. During the analysis of these images, an important observation became apparent. The mean value of the peaks and valleys determined over the total surface area was measured and recorded as the average roughness.

This helped us to identify broad differences in the properties of the overall profile height. The square root of the distribution of surface height is known as the root mean square roughness (RMS R), which is thought to be more sensitive than the average roughness. It displays the profile heights' standard deviation. In particular, each film had RMS R values that were consistently lower than the nominal criterion of 0.3 nm. This overall pattern was a reliable predictor of the crystallinity of the ITO material under the growth conditions of our experiment [10,21,22]. Similar RMS roughness results were found using magnetron sputtering (0.546 nm) [23] and another deposition technique (0.293 nm) [24]. Alternatively, we can see higher RMS roughness values found by Rita M. Carvalho et al. [25] and others [26–28] ranging between 3.9 nm up to 24.8 nm. We attribute these rough ITO surfaces to high temperatures used during growth and annealing as, in one method, they used thermal evaporation which can induce the formation of indium oxide on the surface, creating a clear variation; to the lack of annealing in proper and inert conditions; to the deposition parameters that included the distance between the target and the substrate; and to the gas pressure in the chamber and the sputtering power. Our low RMS roughness values can be attributed to the growth method in a vacuum which hindered the oxidation and formation of rough layers in inert conditions. Moreover, using an inert gas in the annealing method contributed to smoother films as indium tends to oxidize at high temperatures which can increase the formation of random indium oxide particles on the surface.



Figure 4. AFM images of ITO films with different thicknesses and their respective RMS R values.

A recognizable pattern was revealed through further analysis of the RMS R values. In particular, values between 0.2571 nm and 0.2645 nm gradually emerged as the ITO layer's thickness rose, covering the thickness range of 50 nm to 150 nm. However, after reaching a thickness of 200 nm, this pattern underwent a noticeable shift. The measured RMS R levels started to decrease at this point, going from 0.2411 nm to 0.2256 nm for thicknesses of 200 nm to 300 nm. We suggest that this phenomenon can be attributed to the natural transition taking place at the surface, which signaled the emergence of a more refined and smooth ITO film and an increase in grain sizes. The changes shown in Figure 4 resemble this perceptible growth, as the sharpness of the tip ends changed to a more curved layout while simultaneously showing an expansion in the grain dimensions. From our experiment, we can conclude that all the layers had optimal RMS R values and crystalline amorphous structures, which tended to have higher roughness and lower conductivity values. With increased roughness, we acquired a higher conductivity which was a result of the tips being closer to one another which helped in the transitioning of charges on the surface.

In summary, our utilization of atomic force microscopy in the analysis of the ITO films unveiled the intricate relationships between surface morphology, crystallinity, and electrical conductivity [29]. The low RMS R values signified the crystalline nature of the ITO films that were produced under our experimental conditions. The distinct trend of roughness value vs. thickness further solidifies this notion.

3.3. Four-Point Probe

Figure 5a–c show the electrical properties of the ITO films with different thicknesses before and after annealing. It is essential to understand the electrical properties to determine the quality of the deposited ITO [30].



Figure 5. (a) Conductivity (S/m), (b) resistivity (Ω m), and (c) sheet resistance (Ω sq⁻¹) vs. film thickness (nm).

Conductivity is one of the most important properties of an ITO thin film layer in third-generation solar-cell devices. In our films, we found that the conductivity values decreased with increasing thickness and then sharply increased after reaching 200 nm prior to annealing; this can be explained as thicker layers having higher conductivity due to reduced scattering sites and defects. However, thick layers tend to have poor crystallinity. On the other hand, after annealing, the films showed better conductivity values as the grain size increased; therefore, there was less boundary scattering [8], and the recrystallization reduced crystal defects and improved the electron mobility in the lattice [31] with better results at 50 nm and 100 nm (between $1.8-2 \times 10^6$ S/m). It is important to consider that the optimal conductivity for ITO used in optoelectronic materials and solar cells should not be less than 1×10^4 S/m [32]. Another important property for suitable ITO thin films in third-generation solar-cell devices is resistivity. Figure 5b illustrates the resistivity of the ITO samples with different thicknesses before and after annealing. Prior to annealing, the films had a high resistivity which was attributed to the low mobility of charge carriers. Nevertheless, the resistivity was quite stable post-annealing and was in the optimal range for solar-cell applications. A good resistivity for ITO for solar-cell applications is less than $1-2 \times 10^{-6} \Omega m$ [33,34]. In our results, we obtained values of 4×10^{-7} to $9 \times 10^{-7} \Omega m$, indicating an optimal quality for the created films. It can be seen that the lowest and optimal resistivity was measured from the films with thicknesses of 50 nm and 100 nm. Figure 5c shows the pre- and post-annealing sheet resistance values of the samples. Annealing plays an important role in reducing the values of sheet resistance [35] which, in turn, is highly affected by the resistivity and the thickness of the layer. From the figure, we can observe that annealing improved the sheet resistance (R_{sh}). Equation (1) links these variables together:

$$R_{\rm sh} = \frac{\rho}{t} \tag{1}$$

where ρ is the resistivity of the thin film and *t* is the thickness of the thin film. It is expected that with increased thickness, we will have lower sheet resistance values. Nonetheless, the lower sheet resistance of these samples was also associated with a slightly lower conductivity and higher resistivity. Therefore, the optimal thickness based on the electrical properties was 100 nm. We could also opt for 50 nm but the film with this thickness showed a high sheet resistance that might affect the layers grown on the ITO and the efficiency of the solar device. We can conclude that annealing plays an important role in the improvement of ITO thin films [36].

3.4. Scanning Electron Microscopy

Scanning electron microscopy (SEM) was performed to confirm the actual thickness of each layer and to study the influence of the morphology on the optical, electrical, and mechanical properties of the films.

We can see, from the images in Figure 6 and measurements, that the thickness of the films was accurate; this suggests high-precision growth using the radio frequency magnetron sputtering machine: the 50 nm film was measured as 51.6 nm, the 100 nm film was measured as 103.1 nm, and the 150 nm film was measured as 154.6 nm. The analysis revealed a shared characteristic among all the films: a uniform surface structure composed of nucleation sites pointed by white arrows in the figure that decreased in size as the thickness increased; this is because the Volmer–Weber island growth mode shifted to a Frank–van der Merwe mode, which is a transition from a 3D growth mode to a 2D growth mode, when the thickness was increased and the nodes and clusters were transformed into layers. This smoothness, which was free from both empty spaces and fractures, created good conductivity as fractures can contribute to extremely irregular electrical voltages on the surface [37,38].



Figure 6. SEM images of top and cross-section of ITO films with thicknesses of 50, 100, and 150 nm after annealing.

3.5. Optical Properties

The final and most important property of ITO, which enables it to be installed or built into solar devices as the front electrode, is the transparency of the ITO film grown on the glass substrate. Initially, the silica low-iron glass substrate had a transmittance value of 94%. As can be seen in Figure 7, the transparency values prior to annealing were all below 85% [33,39,40], which are very poor transparency values due to the darker color of the ITO and the reflective properties it had before annealing. Furthermore, the post-annealing transparency (Figure 8) increased significantly in all samples with the best values observed in the films with thicknesses of 50 nm, 100 nm, and 150 nm with transparency values of 89%, 86.16%, and 86.92% at wavelengths of 635 nm, 560 nm, and 550 nm, respectively. This result indicates that these are highly transparent films that can be used for third-generation solar-cell applications [41]. Again, annealing the ITO samples was proven to improve the transmittance due to increasing the charge carrier numbers, with a better crystal quality and a decrease in grain boundary scattering as the grain sizes increased with temperature [42]. Although the 150 nm and 50 nm thicknesses showed better transparency values, they had a lower electrical quality compared to the 100 nm film.



Figure 7. Transmittance (%) of films prior to annealing vs. wavelength (nm).



Figure 8. Transmittance (%) of films after annealing vs. wavelength (nm).

Through our examination of the results, we found that the best thickness was 100 nm in terms of physical, electrical, and optical properties. Thus, we calculated the absorbance (A) of this sample using the transmittance data and Equation (2):

$$A = 2 - \log(T\%) \tag{2}$$

Figure 9 illustrates the resulting absorbance which was in the range of 0.1 to 0.2 Abs.u, indicating a highly favorable range [43,44], as the lowest absorbance possible is desirable for the application of electrodes in third-generation solar cells [7,45–47]. We used the absorbance to determine the bandgap using a Tauc plot, as shown in the inset of Figure 9. The resulting bandgap was 3.44 eV [48,49]. We validated the bandgap using the methods used by Jose C.S. Costa et al. [50] and Dariush Souri et al. [51] which indicated that the ITO film had highly transmittance and required the lowest energy from a photon to create voltage in any solar-cell circuit [52–55].



Figure 9. The absorbance of 100 nm ITO thin film with the calculated bandgap in the inset.

To provide more insights into our work, Table 1 summarizes the significant results of this study and compares them to those of previous studies.

Ref.	Year	Gas Type	Thickness (nm)	Annealing Temp (°C)	Electrical Properties	Transparency (%)	Band Gap (eV)	Morphological Properties
F. Kurdesau et al. [10]	2006	Argon– Oxygen	300–500	-	-	80-85	-	SEM: small-grained (10–20 nm) structure
Vinh Ai Dao et al. [8]	2010	Argon	100 ± 5	100	-	87–90	3.67–3.83	-
D Kudryashov et al. [13]	2013	Argon	~100	-	$\begin{array}{c} \text{Resistivity:} \\ 5.4\times10^{-4}~\Omega{\cdot}\text{cm} \end{array}$	80–90	-	Smooth surface
A. P. Amalathas et al. [11]	2016	Argon	75–225	-	Average resistivity: $9.4 \times 10^{-4} \ \Omega \cdot cm$	Over 75	3.831-4.003	AFM: surface roughness increased with thickness
Shumin Yang et al. [12]	2020	Oxygen	~150	300	-	89.02–90.7	3.60-3.67	-
This work	2024	Argon	100	500	Resistivity range: $1-2 \times 10^{-4} \ \Omega \cdot cm$	86.16-89.0	3.44	Low RMS roughness values

Table 1. A comprehensive comparison between this work and previous studies.

4. Conclusions

In our recent research conducted at the ESI labs, we explored the growth of indium tin oxide (ITO) thin films using RF magnetron sputtering with argon gas. This approach is relevant for optoelectronic applications, particularly for third-generation solar cells. Through the various film thicknesses tested, we discovered that the films exhibited exceptional physical, electrical, and optical properties. However, the optimal thickness was identified as 100 nm. This particular thickness was distinguished by its remarkable transparency, exceeding 86%; low absorbance, ranging between 0.1 to 0.2 Abs.u; good bandgap energy of 3.44 eV coupled with superior electrical conductivity reaching about 1.86×10^6 S/m; and low resistivity values of approximately $5.3 \times 10^{-7} \Omega m$. These characteristics are crucial for ensuring the efficiency of optoelectronic devices used in the field of third-generation solar cells. Our SEM analysis confirmed that the surface morphology of these films was crack-free and validated the thicknesses achieved. Additionally, the ATM assessments indicated a uniform and gradual growth of the thin films with excellent RMS roughness values. Furthermore, the XRD analyses provided insights into the crystalline structure of the films, affirming their suitability for third-generation solar-cell applications. This research underscores the efficiency of RF magnetron sputtering in creating high-quality ITO films, with the 100 nm film particularly demonstrating promising properties for future technological innovations and competing with commercial ITO.

Author Contributions: Methodology, investigation, formal analysis, software, validation, writing original draft, and resources, H.I.A.; methodology, investigation, formal analysis, validation, and writing—review and editing, F.M.A.; conceptualization, validation, writing—review and editing, and visualization, S.B.; conceptualization, writing—review and editing, supervision, project administration, and funding acquisition, T.M. All authors have read and agreed to the published version of the manuscript.

Funding: The work is partially funded through Engineering and Physical Science Research Council (EP/S030786/1) funded End Use Energy Demand Technology projects to the University of Exeter. For the purpose of open access, the author has applied a Creative Commons Attribution (CC BY) license to any Author Accepted Manuscript version arising from this submission.

Data Availability Statement: The data presented in this study are available upon request from the corresponding author.

Acknowledgments: H. Alabdan and F. Alsahli would like to duly acknowledge the financial support of the Saudi Arabia Culture Bureau in the United Kingdom. The authors thank Dr Hong Chang, Imaging Suite Manager at the Harrison Building, University of Exeter, Streatham Campus, U.K., for their training and technical assistance with the SEM, AFM, and XRD characterizations.

Conflicts of Interest: The authors declare no conflicts of interest and the funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript; or in the decision to publish the results.

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Article



Thermal Stability and Crystallization Processes of $Pd_{78}Au_4Si_{18}$ Thin Films Visualized via In Situ TEM

Bingjiao Yu¹, Rui Zhao², Zhen Lu², Hangbo Su¹, Binye Liang¹, Bingjie Liu³, Chunlan Ma⁴, Yan Zhu³ and Zian Li^{1,*}

- ¹ State Key Laboratory of Featured Metal Materials and Life-Cycle Safety for Composite Structures, School of Physical Science and Technology, Guangxi University, Nanning 530004, China; 2107301168@st.gxu.edu.cn (B.Y.); 2007301124@st.gxu.edu.cn (H.S.); 2207301068@st.gxu.edu.cn (B.L.)
- ² Institute of Physics, Chines Academy of Sciences, Beijing 100190, China; zhaorui@iphy.ac.cn (R.Z.); zhenlu@iphy.ac.cn (Z.L.)
- ³ MIIT Key Laboratory of Aerospace Information Materials and Physics, College of Science, Nanjing University of Aeronautics and Astronautics, Nanjing 211106, China; IllIlbj@nuaa.edu.cn (B.L.); yzhu@nuaa.edu.cn (Y.Z.)
- ⁴ Jiangsu Key Laboratory of Micro and Nano Heat Fluid Flow Technology and Energy Application, School of Mathematics and Physics, Suzhou University of Science and Technology, Suzhou 215009, China; wkmcl@usts.edu.cn
- * Correspondence: zianli@gxu.edu.cn

Abstract: Amorphous alloys or metallic glasses (MGs) thin films have attracted extensive attention in various fields due to their unique functional properties. Here, we use in situ heating transmission electron microscopy (TEM) to investigate the thermal stability and crystallization behavior of Pd-Au-Si thin films prepared by a pulsed laser deposition (PLD) method. Upon heating treatment inside a TEM, we trace the structural changes in the Pd-Au-Si thin films through directly recording highresolution images and diffraction patterns at different temperatures. TEM observations reveal that the Pd-Au-Si thin films started to nucleate with small crystalline embryos uniformly distributed in the glassy matrix upon approaching the glass transition temperature $T_g = 625$ K, and subsequently, the growth of crystalline nuclei into sub-10 nm Pd-Si nanocrystals commenced. Upon further increasing the temperature to 673 K, the thin films transformed to micro-sized patches of stacking-faulty lamellae that further crystallized into Pd₉Si₂ and Pd₃Si intermetallic compounds. Interestingly, with prolonged thermal heating at elevated temperatures, the Pd₉Si₂ transformed to Pd₃Si. Simultaneously, the solute Au atoms initially dissolved in glassy alloys and eventually precipitated out of the Pd₉Si₂ and Pd₃Si intermetallics, forming nearly spherical Au nanocrystals. Our TEM results reveal the unique thermal stability and crystallization processes of the PLD-prepared Pd-Au-Si thin films as well as demonstrate a possibility of producing a large quantity of pure nanocrystals out of amorphous solids for various applications.

Keywords: nanometallic glasses; crystallization processes; in situ TEM

1. Introduction

Amorphous alloys or metallic glasses (MGs) represent a unique class of materials that possess an overall glassy atomic structure free of crystalline grains and lattice defects [1]. The non-crystalline nature makes them exhibiting superior mechanical or functional properties, such as exceptionally high strength, hardness, wear and corrosion resistance, and thermoplastic processability [2–4]. In addition to the fast development in bulk MGs, recent developments in this field also witness a rapid progress of nanoscale MGs [5] in the form of thin films or nanowires [6] or nanoparticles (NPs) [7]. However, nanoscale MGs are metastable materials being prone to crystallization when subjected to thermal treatments. To retain their glassy structures and outstanding properties, it is imperative to prevent crystallization during the heat-involved processing of nanoscale MGs at elevated

Citation: Yu, B.; Zhao, R.; Lu, Z.; Su, H.; Liang, B.; Liu, B.; Ma, C.; Zhu, Y.; Li, Z. Thermal Stability and Crystallization Processes of Pd₇₈Au₄Si₁₈ Thin Films Visualized via In Situ TEM. *Nanomaterials* **2024**, *14*, 635. https://doi.org/10.3390/ nano14070635

Academic Editor: Andrey Chuvilin

Received: 11 March 2024 Revised: 28 March 2024 Accepted: 1 April 2024 Published: 5 April 2024



Copyright: © 2024 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). temperatures. Therefore, understanding thermal stability and crystallization processes in nanoscale MGs is of critical importance for both the fundamental and applied research. From a different perspective, nanoscale MGs could also be used as precursor materials for producing crystalline nano-sized alloys, which also requires an in-depth understanding of crystallization processes of nanoscale MGs. For examples, the free surface of a nanoscale MG acts as the heterogeneous nucleation site for crystallization, because the surface atoms are in higher energy states than the interior atoms [7,8].

Previous experiments employing various forms of broad-beam-based (light or X-ray or neutron) techniques provide macroscopically averaged information about the bulk metallic glasses [9]. However, the finite dimensions and limited volume of nanoscale metallic glasses present great challenges in probing their thermal stability and crystallization processes. In contrast, in situ transmission electron microscopy (TEM) techniques can simultaneously activate and visualize structural changes, and they have been used to observe the dynamic structural changes of nanomaterials, such as the growth of nanocrystals [10] and nanowires [11], and phase transformations in glassy materials [12,13], providing a near atomic understanding of their underlying mechanisms. Recent in situ heating TEM experiments have been used to study the crystallization behavior of MG nanorods and have revealed the finite-size effect on the apparent onset of crystallization [6]. Moreover, the viscous flow of amorphous materials and activation effects caused by electron irradiation in TEM were reported previously [14].

In this work, we use in situ heating TEM to investigate the thermal stability and crystallization processes of Pd-Au-Si thin films prepared by pulsed laser deposition, particularly focusing on the effect of Au substitution on Pd in the eutectic composition Pd-Si thin films. The crystallization kinetics of eutectic Pd82Si18 and its Au-substituted Pd78Au4Si18 bulks have been thoroughly investigated, but these are mainly focusing on the temperature range around the glass transition temperature [15-17]. With new development in thin film preparation, various amorphous solids or metallic glasses can be prepared in the form of thin films or further reduced dimensions [5,18,19]. Therefore, studies of the thermal stability and crystallization processes of thin films become important yet challenging topics because conventional methods suitable for bulks are difficult to apply on thin films. Here, we employ in situ heating TEM experiments to investigate their thermal stability and crystallization behaviors. We aim to reveal the effects of thin film and the Au substitution on the crystallization of the PLD-prepared eutectic Pd₇₈Au₄Si₁₈ thin films. We first trace the crystal nucleation and growth in thin films at moderate temperatures around the glass transition temperature T_g . We then raise the specimen temperature well above the T_g to observe the crystal phase transformation and Au precipitation in the Pd₇₈Au₄Si₁₈ system. The observed precipitation of Au nanocrystals out of PLD-prepared Pd₇₈Au₄Si₁₈ thin films may exemplify an efficient route to prepare pure nanocrystals with a large quantity for various applications.

2. Materials and Methods

Pd-Au-Si metallic glass thin films were fabricated by a pulsed laser deposition (PLD) method. The thin films were directly deposited on rotating NaCl substrates inside a vacuum chamber with a base pressure of 2×10^{-5} Pa. The target of composition Pd_{85.5}Au₃Si_{11.5} (in atomic percent) was ablated by excimer KrF laser pulse ($\lambda = 248$ nm, t = 25 ns) at a laser repetition of 8 Hz. Prior to deposition, the target was ablated for 4 min. The film thickness (ranging from 10 to 1000 nm) can be finely controlled by regulating the duration time of deposition. The as-deposited thin films were detached from NaCl substrates by dissolving the NaCl in deionized water. The free-standing films were then transported to 1000-mesh Ni-grids for TEM characterization. TEM experiments were conducted via two electron microscopes (Environmental Titan TEM G2 80-300 working at 300 kV, and Talos F200X G2 working at 200 kV, and both from Scientific Fischer Inc., Hampton, NH, USA. High-angle annular dark-field (HAADF) imaging and energy dispersive X-ray spectroscopy (EDXS) measurements were conducted in both microscopes. The use of a heating holder (model

652.IN, Gatan Inc., Pleasanton, CA, USA) allows the specimen temperature to be varied from room temperature up to 1000 K. In the heating TEM experiments, the heating rate is set at about 2 K min⁻¹, and the specimens are placed under the vacuum of about 2×10^{-5} Pa via an electron microscope.

Calculations of binding energies for Pd₉Si₂ and Pd₃Si intermetallics were carried out with self-consistent density functional theory (DFT) in the Vienna Ab initio Simulation package (VASP) [20–22]. The Perdew–Burke–Ernzerhof (PBE) functional of the generalized gradient approximation (GGA) is imposed for the exchange correlation functional [23]. The plane wave cutoff energy is chosen as 350 eV, and the convergence condition for energy and force are 1×10^{-6} eV, and 1×10^{-2} eV/Å, respectively. In optimizing the structures, the selected k-points for sampling the Brillouin zone are $7 \times 5 \times 7$ and $7 \times 9 \times 7$ for Pd₃Si and Pd₉Si₂, respectively.

3. Results

3.1. Structural Characterization of As-Deposited Pd₇₈Au₄Si₁₈ Film

The structural and the compositional characteristics of the as-deposited $Pd_{78}Au_4Si_{18}$ films were characterized through TEM measurements. Figure 1a,b display a representative bright-field TEM image and the corresponding selected area electron diffraction (SAED) pattern of $Pd_{78}Au_4Si_{18}$ thin film taken from a circular area of a diameter about 800 nm. In this sub-micron scale, the overall amorphous nature of $Pd_{78}Au_4Si_{18}$ thin films is confirmed. In sub-nanoscale, high-resolution TEM (HRTEM) and nanobeam electron diffraction (NBED) measurements were conducted. Figure 1c presents a typical HRTEM image, in which a long-range lattice is absent while lattice patterns (marked by circles) of a few nanometers are observed, which are indicative of short-range crystalline ordering within the thin film. The presence of quenched-in crystalline nuclei is further confirmed by the weak reflections in the NBED pattern [24,25], as shown in Figure 1d. Prior to in situ heating TEM experiments, the overall amorphous while locally short-range crystalline nature of $Pd_{78}Au_4Si_{18}$ free-standing thin films is established.



Figure 1. TEM characterization of amorphous $Pd_{78}Au_4Si_{18}$ metallic glass thin films. (a) Bright-field TEM image survey and (b) typical SAED pattern of metallic glass phase. (c) HRTEM image with short-range ordered regions marked by white circles. (d) NBED pattern and the weak reflections marked by arrows owing to the presence of short-range ordered crystallites.

3.2. Crystallization Processes of Pd78Au4Si18 Films via In Situ TEM

We conducted in situ heating TEM experiments on the $Pd_{78}Au_4Si_{18}$ thin films supported on a Ni grid. Figure 2 shows a typical series of TEM images recording the process of heating up the specimen from room temperature (Figure 2a) to about 1000 K. Upon reaching 653 K (380 °C), very fine crystallites began to nucleate out of the glassy film, as seen in Figure 2b. It is worth noting that the nucleation process is kinetically rather slow when the specimen temperature was kept below 653 K. In other words, neither the number of crystalline nuclei nor their sizes exhibit substantial change over a few hours.



Figure 2. Crystallization processes of $Pd_{78}Au_4Si_{18}$ thin films observed via in situ heating TEM. (a) Initial amorphous state at room temperature. Early stages of homogeneous nucleation and subsequent growth of nanocrystallites at (b) 653 ± 1 K and (c) at 663 ± 1 K. (d–f) are the continuous growth of crystallites into lamella-like stacking faults of PdSi_x (denoted as yellow dashed region). (g–i) With elevated temperature and prolonged heat duration, intermediate phase PdSi_x transforms to Pd₃Si and Pd₉Si₂, and finally to Pd₃Si, along with the precipitation of Au nanocrystals at 973 K.

With further increasing specimen temperature, one can observe a rapid growth of sub-10-nm crystallites (Figure 2c at 663 K) and the emergence of sub-micron-size patches of tweed-like contrast (Figure 2d at 673 K). These tweed-like patches are non-stoichiometric crystalline PdSi_x with a high density of stacking faults, which will transform to stoichiometric Pd₉Si₂ or Pd₃Si phases upon further increasing the specimen temperature, as seen in Figure 2e–h with indicated temperatures. Note that the thermally-driven transformation process of tweed-like patches to crystalline Pd₉Si₂ and Pd₃Si phases will be thoroughly examined below in Figures 3 and 4, respectively. Upon increasing the specimen temperature above 973 K, the tweed-like structure completely turned to highly crystalline Pd₉Si₂ or

Pd₃Si phases [26–28], as seen in Figure 2i. Interestingly, Figure 2i also shows the presence of 100 nm particles that are proved to be pure Au precipitating from the original Pd(Au)-Si crystalline film, which will be thoroughly described below. The whole process of thermal heating was recorded in Supplementary Video S1.



Figure 3. Transformation of metastable PdSi_x phase to stable Pd₉Si₂ phase. (**a**) Bright-field TEM image of coexistence of two phases. Letter A marks the stacking-faulted PdSi_x phase, letter B marks the Pd₉Si₂ single-crystal phase, and white arrows denote the growth direction of Pd₉Si₂. (**b**) HRTEM lattice image and (**c**) corresponding SAED pattern of lamellae area A. Central part of SAED is shown as inset. (**d**) HRTEM lattice image and (**e**) corresponding SAED pattern of Pd₉Si₂ area B. In (**e**) b* denotes the reciprocal axis.

Despite the fact that all of the crystallization processes can be visualized at the nanoscale via in situ TEM and the exact determination of the resultant crystalline phases, some key parameters regarding the crystallization kinetics [29–31] are difficult to estimate,

which is in part due to the lack of fine control over the heating rate. Future studies of in situ TEM techniques with improved fine control over the heating rate will address these difficulties. Instead, we emphasize the direct observation of crystallization processes via in situ TEM and the accurate determination of resultant Pd-Si phases as well as the precipitation of pure Au nanocrystals.



Figure 4. Transformation of metastable PdSi_x phase to stable Pd₃Si phase. (**a**) Bright-field TEM image of coexistence of two phases. Letter A marks the stacking-faulted PdSi_x phase, letter B marks the Pd₃Si single-crystal phase, and white arrows denote the growth direction of Pd₃Si. (**b**,**c**) are the HRTEM lattice images and the corresponding SAED patterns of area A. Central part of SAED is shown as inset. (**d**) Bright-field image of Figure (**a**) completely transformed into the Pd₃Si phase. (**e**,**f**) are the HRTEM lattice images and the corresponding SAED patterns of area B. In (**f**) a* and b* denote the reciprocal axes.

3.3. Transformation of Metastable Pd-Si to Stable Pd₉Si₂ and Pd₃Si

We proceed to examine the tweed-like metastable $PdSi_x$ phase with high-density planar defects and their transformation to stoichiometric Pd_9Si_2 and Pd_3Si single-crystal phases upon further thermal heating. Figure 3a shows a distinct grain boundary separating two regions marked by A and B. In region A of the $PdSi_x$ phase, Figure 3b depicts a highresolution TEM lattice image with high-density stacking faults, which cause the streaking reflections in the corresponding SAED pattern in Figure 3c. Note that it remains a challenge to determine the exact crystal structure and chemical composition of the metastable $PdSi_x$ phase because of its metastable and faulty lattice. Previous studies reported that the metastable $PdSi_x$ structure could be either monoclinic or triclinic unit cells [17,32,33]. These stacking faults are of higher energy and will tend to transform into a lower energy state upon prolonged thermal treatment. Then, the transition can occur from a stacking fault crystal (region A in Figure 3a) toward a single crystal structure (region B in Figure 3a) along the direction indicated by the white arrows, which corresponds to the (0 2 0) crystal plane in the SAED pattern along the [1 0 $\overline{1}$] zone axis. (Figure 3e). It indicates that Pd_9Si_2 grows along the low-order [0 1 0] direction by the nucleation and propagation of unit-cell ledges on the (0 1 0) planes.

In region B of the Pd₉Si₂ single phase, Figure 3d,e represent the $[1 \ 0 \ \overline{1}]$ -oriented high-resolution TEM lattice image and their corresponding SAED pattern. The growth direction of Pd₃Si was also determined to be $[0 \ 1 \ 0]$, initiating and propagating on the $(0 \ 1 \ 0)$ planes [34]. Figure 4a,d represent the metastable PdSi_x phase and Pd₃Si single-crystal phase. Figure 4b,c are the high-resolution lattice image and the SAED pattern of the metastable phase, where Figure 4e,f depict the Pd₃Si single-crystal phase. Note that the Pd₉Si₂ and Pd₃Si intermetallics were also previously reported to be stable down to room temperature [28,35].

3.4. Growth of Pd₃Si at the Expense of Pd₉Si₂

Figure 5a shows a typical TEM image of a mixture of Pd_9Si_2 and Pd_3Si crystalline phases. Analyses of SAED patterns allow one to identify the particular structure for each grain, as shown in Figure 5a, where 9-2 marks the Pd_3Si grain, 3-1 marks the Pd_3Si grain, and yellow-dashed lines mark the grain boundaries. The areas in Pd_9Si_2 grains denoted by letters A and B were selected for recording SAED patterns, as shown in Figure 5b,c, respectively. The sharp and bright reflections in both SAED patterns suggest the single crystal nature of the Pd_9Si_2 grains.

With prolonged isothermal heat treatment, we observed a phase transformation of Pd₉Si₂ into Pd₃Si: namely, a continuous growth of Pd₃Si at the expense of Pd₉Si₂. To visualize directly the Pd₉Si₂ to Pd₃Si transformation, we track the same area by recording TEM images during isothermal heating. Figure 5d shows the same area as marked in Figure 5a, and the regions marked by C and D correspond to A and B in Figure 5a. The SAED patterns for regions C and D are shown in Figure 5e,*f*, respectively. These SAED patterns can be indexed with the Pd₃Si structure, demonstrating that the original Pd₉Si₂ grains have transformed to Pd₃Si grains. The growth directions of continuous Pd₃Si grains at the expense of Pd₉Si₂ ones are indicated by white arrows in Figure 5a. The detailed transformation process is given in the Supplementary Video S2.

3.5. Precipitation of Au NPs at Elevated Temperatures

In addition to the formation of micron-sized Pd₃Si grains, near-spherical-shaped NPs are observed in Figure 5a,d during prolonged isothermal heating above 873 K (or 600 °C). We carried out HAADF imaging and EDXS mapping to characterize these NPs. Figure 6a shows a typical HAADF image of NPs distributed in the Pd₃Si grains. Since HAADF intensity scales with the atomic number Z of constituent elements, the brighter contrast of NPs can be attributed to the high atomic number of Au (Z = 79). Figure 6b,c represent the NBED pattern and the HRTEM lattice image of individual Au NPs, indicating their highly crystalline phase. Figure 6d–f show the EDXS mapping for the constituent elements of Pd, Si, and Au, respectively, which unambiguously reveal the precipitation of Au NPs out of the Pd₇₈Au₄Si₁₈ thin films upon thermal heat treatment. The EDXS maps of Au (Figure 6f) were used to calculate the Au nanoparticle size distribution, as shown in Figure 6g. This size distribution follows a log-normal distribution with a mean value of 124 ± 5 nm. Note that some of the Au NPs in Figure 6f exhibit elongated shapes rather than spherical ones because of their coalescence and Ostwald ripening in prolonged thermal treatment. With



fine control over the thermal treatment temperature and duration time, we can obtain a nearly spherical shape of Au NPs well dispersed in the Pd_3Si single-crystal thin films.

Figure 5. Continuous growth of Pd₃Si at the expense of Pd₉Si₂ during prolonged isothermal heat treatment. (**a**) Bright-field TEM image of coexistence of Pd₃Si marked by 3-1 and Pd₉Si₂ marked by 9-2. Yellow-dash lines denote the phase boundaries, white arrows denote the growth direction of Pd₃Si, letters A and B mark the Pd₉Si₂ regions, and the corresponding SAED patterns are shown in (**b**,**c**), respectively. (**d**) Identical area as (**a**) but after the complete growth of Pd₃Si. Note that the areas C and D mark the respective areas A and B in (**a**), and their corresponding SAED patterns are shown in (**e**,**f**). Note that (**c**,**e**,**f**) share the same scale bar in (**b**).

To understand the Au precipitating out of Pd-Si thin film, we check the mixing enthalpy for a ternary compound system. According to the No. 104 entry of Table 1 in the work [36] presented by Takeuchi and Inoue, the mixing enthalpy ΔH^{mix} in unit of $(kJ \cdot mol^{-1})$ values of Au-Pd-Si subsystems calculated based on Miedema's macroscopic model are 0 for Au-Pd, -30 for Au-Si, and -55 for Pd-Si. Since the Au content is a minor part in the eutectic alloy of Pd₇₈Au₄Si₁₈, upon heating, it tends to crystallize into Pd₉Si₂ and Pd₃Si, and consequently, the solute Au elements tend to precipitate to form nanocrystals at elevated temperatures.



Figure 6. Precipitation of Au NPs characterized via HAADF imaging and EDXS. (**a**) HAADF survey image displays the Au NPs. (**b**) HRTEM lattice image and (**c**) the corresponding nanobeam electron diffraction pattern of Au nanoparticles. EDXS spectroscopic mapping for (**d**) Pd, (**e**) Si, and (**f**) Au elements. (**g**) Fitting of a log-normal function to the size distribution of Au NPs.

4. Discussion

4.1. Effects of Quenched-in Nuclei on Crystallization Processes of Pd-Au-Si Thin Films

It is now well-documented [17,37,38] that in metal–metalloid amorphous alloys, there exist short- and medium-range-ordered crystallites with rich atomistic motifs depending on many intrinsic (composition) or extrinsic (fabrication and processing) factors. These quenched-in ultrafine crystallites play critical roles in the nucleation and subsequent growth of crystals out of amorphous alloys. In this work, we also detected the presence of nanoscale

crystallites uniformly distributed in the PLD-deposited Pd-Au-Si thin films, and we observed the incipient crystallization commencing around the quenched-in crystallites at relatively low temperatures (see Figure 1). The presence of quenched-in crystallites also explains partially the lower transition and initial crystallization temperatures T_g and T_x in comparison to the arc-melt bulk MGs and melt-spun ribbons [16,28,39,40].

The lamellar structures observed in our PLD-prepared thin films have been reported in previous TEM experiments. For example, Masumoto et al. [41] first reported that at the beginning of crystallization, the MS-I phase precipitated out from the amorphous matrix. Upon increasing the annealing temperature, the MS-I phase then transformed to the MS-II phase, which finally reached the equilibrium Pd₃Si phase. According to Masumoto et al. [41], MS-I is a Pd-Si solid solution which has a FCC unit cell with a = 0.40 nm, and MS-II is an unknown complex superlattice structure. Duhaj et al. [42] reported that the complex appearance of MS-II might be attributed to the morphology of mixed Pd₉Si₂ and Pd₃Si phases at various temperatures. Brearley et al. [34] investigated the lamellar structure of mixed Pd₉Si₂ and Pd₃Si phases. Wu et al. [28] claimed that the morphologically complex MS-II phase can be formed in the whole amorphous formation region in the Pd-Si system displaying various crystallization processes involving transition states and phase transformation. These lamellar structures are also observed in our TEM experiments on the PLD-prepared Pd-Au-Si thin films and exhibit many similar crystallization behaviors and phenomena.

4.2. Transformation of Pd₉Si₂ to Pd₃Si at Elevated Temperatures

To understand the Pd₉Si₂ to Pd₃Si transformation above 923 K in the PLD-prepared Pd-Au-Si thin films, we consider their atomic structures, binding energies and thermodynamic properties. Both Pd₉Si₂ and Pd₃Si share a common orthorhombic atomic structure with a space group Pnma [27,43]. Note that structurally, the Pd₉Si₂ phase is somewhat related to Pd₃Si; namely, it is a superlattice which contains four times as many Pd atoms (48 total) as Pd₃Si with the Si atoms randomly occupying only 11 of the 16 possible z = 1/4and 3/4 sites [27]. The metal-metalloid bonding is considerably more isotropic than that in Pd₃Si [34]. We performed DFT calculations using a VASP software on the structural optimization and binding energy evaluation of both Pd₉Si₂ and Pd₃Si (calculation details are given in the Materials and Methods section). Starting from experimental crystal structures, we change the scaling coefficient to perform a series of structural relaxations. Selecting the result with the lowest energy, subtle adjustments based on the lattice constant in the minimum direction are further carried out to identify the lowest-energy structure. The calculated lattice parameters for both phases at equilibrium are listed in Table 1.

	a (Å)	b (Å)	c (Å)	V (Å ³)	$E_{Pd_nSi_m}$ (eV)	\mathbf{E}_{B}^{bulk} (eV)	E_{BV}^{bulk} (meV/Å ³)
Pd ₃ Si	5.934	7.639	5.350	242.529	-93.6	-9.8	-40.2
Pd_9Si_2	9.263	7.616	9.659	681.417	-249.8	-20.0	-29.4

Table 1. The DFT calculations of lattice constants and binding energies of Pd₃Si and Pd₉Si₂.

With the structure optimization results, one can calculate the binding energy as $E_B = E_{Pd_nSi_m} - E_{Pd_n} - E_{Si_m}$. The total binding energy of the Pd_nSi_m structure is $E_{Pd_nSi_m}$, and E_{Pd_n} and E_{Si_m} are the energies in their respective equilibrium bulk phases. The resultant binding energies are summarized in Table 1. Since their compositions are very different, it is informative to compare the binding energies per unit volume $E_{BV} = \frac{E_B}{V}$, as tabulated in Table 1. The binding energy for the Pd_3Si phase is 10.8 meV Å⁻³ lower than that of the Pd_9Si_2 phase, suggesting that Pd_3Si is energetically stable over the Pd_9Si_2 phase at zero-temperature.

It is worth noting the melting temperatures (T_m) for Pd₃Si of 1318 K and Pd₉Si₂ of 1096 K, suggesting their inherent thermal stability [34]. Here, our TEM experiments reveal that the Pd₉Si₂ to Pd₃Si transformation occurred around 823 K, which is significantly lower

compared to $T_m = 1096$ K of bulk Pd₉Si₂. The large portion of atoms at the surfaces of thin films may help reduce the melting temperature.

4.3. Precipitation of Au NPs from Crystallization of Amorphous Pd-Au-Si System

During the formation of Pd₉Si₂ and Pd₃Si intermetallics in the Pd₇₈Au₄Si₁₈ thin films at high temperatures above 923 K, the Au atoms simultaneously precipitated out of the Pd-Si crystals to form Au NPs. These Au NPs uniformly dispersed in the self-standing thin films upon the completion of Pd₃Si crystallization. When the specimen temperature further increases, the isolated Au NPs become mobile and tend to coalesce into larger NPs. To understand the precipitation phenomenon of Au out of the ternary Pd-Au-Si thin films at evaluated temperature, it is informative to check their binary Au-Pd, Au-Si and Pd-Si phase diagrams. In the Au-Pd phase diagram, these elements form solid solution across the whole composition range. By contrast, there exits a limited solubility in Au-Si phase diagram, and there exist several intermetallic compounds including Pd₅Si, Pd₉Si₂, Pd₃Si and Pd₂Si in the Pd-Si phase diagram [44,45]. In the as-prepared Pd₇₈Au₄Si₁₈ system, the content of Au is about 4 at.% as minor solute elements. At elevated temperature, the Pd-Si crystallized into Pd₉Si₂ and Pd₃Si intermetallics, while the small amount of solute Au elements precipitated into crystalline NPs. It is worth noting that in our TEM experiments, the $Pd_{78}Au_4Si_{18}$ thin films are kept in a vacuum of 2×10^{-5} Pa, and in the magnetic field, they are kept in a vacuum of around 2 T.

It remains an open question regarding the nanoscale effect (finite thickness) of thin films on the crystallization processes as well as the influence of specific TEM vacuum and magnetic-field conditions during heating treatment. Previous reports suggest that the sublimation of metals or alloys can occur in TEM heating experiments at temperatures significantly lower than their respective melting temperatures [46,47].

Our survey of literature suggests that this study provides the first report of the precipitation of Au NPs out of the Pd-Au-Si ternary systems. Previous investigations of the Pd_{82-x}Au_xSi₁₈ ternary system largely focused on the crystallization processes below or close to T_g and revealed a rich thermal behaviors of Pd-Au-Si melt-spun ribbon or arc-melt bulk [16,48,49]. Here, our in situ heating TEM experiments allow the specimen temperature to reach around 1000 K, enabling the observation of the precipitation of Au out of Pd-Au-Si amorphous thin films around such elevated temperatures. This precipitation mechanism in amorphous thin films could be further extended to prepare pure noble metal nanoparticles or clusters with a large quantity for a range of applications.

5. Conclusions

In summary, we used a pulsed laser deposition method to prepare Pd-Au-Si amorphous thin films on NaCl substrates and obtained free-standing thin films supported on the Ni-grid by dissolving the NaCl substrates. Prior to in situ heating TEM experiments, the structural and compositional characteristics of the thin films were carefully checked, revealing the compositional $Pd_{78}Au_4Si_{18}$ with the presence of quenched-in nanoscale crystallites. Thermal TEM experiments were then conducted to investigate the thermal evolution and crystallization processes of the $Pd_{78}Au_4Si_{18}$ thin films. Upon heating at various temperatures, TEM observations reveal that the incipient crystallization initiated at around 653 ± 5 K, and the 1–3 nm crystallites grew up to sub-10 nm upon reaching 663 K. As the specimen temperature reached 673 K, sub-micron lamellae structures emerged and rapidly engulfed the pre-formed crystallites until the temperature reached 723 K. As specimen temperature increased to 823 K, the metastable lamellar structures transformed to Pd₉Si₂ and Pd₃Si intermetallics. Furthering the specimen temperature to 823 K, the Pd₃Si crystals continued growth at the expense of Pd₉Si₂. Around such elevated temperatures, the Au nanocrystals simultaneously precipitated out of the Pd-Au-Si solid solution.

The Pd₇₈Au₄Si₁₈ amorphous alloy undergoes multiple steps of atomic diffusion and rearrangement during thermal heating, gradually transitioning from an amorphous state to crystalline Pd₃Si and Pd₉Si₂ intermetallic compounds and precipitating pure Au NPs at

higher temperatures. It is worth noting that at higher temperatures, Pd_9Si_2 transformed into the Pd_3Si intermetallic phase in the PLD-prepared $Pd_{78}Au_4Si_{18}$ thin films, which was not reported in previous studies. We attribute the Au precipitation phenomenon to the large negative enthalpy of Pd and Si to form intermetallics, while the Pd-Au or Au-Si do have relatively small negative enthalpy; in turn, pure Au precipitates out of the Pd-Si system. This effect can be further exploited to prepare pure single-element metal or alloy nanocrystals uniformly dispersed on supporting amorphous or crystalline solids.

Supplementary Materials: The following supporting information can be downloaded at: https: //www.mdpi.com/article/10.3390/nano14070635/s1. Figure S1: The final products of heating treatment of Pd₇₈Au₄Si₁₈ thin film at around 900 K; Figure S2: HAADF-STEM image and EDXS mappings of the Pd₇₈Au₄Si₁₈ thin film at different temperatures; Video S1: The whole process of heating treatment of Pd₇₈Au₄Si₁₈ thin film inside a TEM; Video S2: The transformation process of Pd₉Si₂ to Pd₃Si intermetallic phases.

Author Contributions: Conceptualization, B.Y., R.Z. and Z.L. (Zian Li); methodology, B.Y., Y.Z. and Z.L. (Zhen Lu); software, B.L. (Bingjie Liu), C.M. and Y.Z.; validation, B.Y., Y.Z. and Z.L. (Zhen Lu); formal analysis, B.Y., H.S. and B.L. (Bingjie Liu); investigation, B.Y., B.L. (Binye Liang) and Z.L. (Zhen Lu); resources, Y.Z. and Z.L. (Zian Li); data curation, B.Y., R.Z. and B.L. (Binye Liang); writing—original draft preparation, B.Y.; writing—review and editing, B.Y. and Z.L. (Zian Li); supervision, R.Z. and Z.L. (Zian Li); project administration, Z.L. (Zian Li); funding acquisition, Z.L. (Zian Li). All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by the National Natural Science Foundation of China (Nos. 12364018 and 11974019), Guangxi Science and Technology Major Program (No. AA23073019) and the Innovation Project of Guangxi Graduate Education (Nos. YCBZ2022049 and YCBZ2023015).

Data Availability Statement: The data presented in this study are available on request from the corresponding author.

Acknowledgments: The Center for Instrumental Analysis of Guangxi University is acknowledged for providing research facilities and resources for the experiments.

Conflicts of Interest: The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Abbreviations

The following abbreviations are used in this manuscript:

TEMtransmission electron microscopySAEDselected area electron diffractionHRTEMhigh-resolution TEMNBEDnanobeam electron diffractionPLDpulse laser deposition

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Article MnO/ZnO:Zn Thin-Film Frequency Adaptive Heterostructure for Future Sustainable Memristive Systems

Karen A. Neri-Espinoza^{1,*}, José A. Andraca-Adame^{1,*}, Miguel A. Domínguez-Crespo¹, Francisco Gutiérrez-Galicia¹, Roberto Baca-Arroyo², Héctor J. Dorantes-Rosales³ and Ramón Peña-Sierra⁴

- ¹ Department of Nanomaterials, Unidad Profesional Interdisciplinaria de Ingeniería Campus Hidalgo (UPIIH), Instituto Politécnico Nacional (IPN), Hidalgo 42162, Mexico; mdominguezc@ipn.mx (M.A.D.-C.); fgutierrezga@ipn.mx (F.G.-G.)
- ² Department of Electronics, Escuela Superior de Ingeniería Mecánica y Eléctrica (ESIME), Instituto Politécnico Nacional (IPN), Mexico City 07738, Mexico; rbaca02006@yahoo.com.mx
- ³ Department of Metallurgical and Materials Engineering, Escuela Superior de Ingeniería Química e Industrias Extractivas (ESIQIE), Instituto Politécnico Nacional (IPN), Mexico City 07738, Mexico; hectordorantes@vahoo.com
- ⁴ Department of Electrical Engineering, Sección de Electrónica de Estado Sólido (SEES), Center for Research and Advanced Studies of the National Polytechnic Institute (CINVESTAV-IPN), Mexico City 07360, Mexico; rpsierra@cinvestav.mx
- * Correspondence: kneri@ipn.mx (K.A.N.-E.); jandraca@ipn.mx (J.A.A.-A.)

Abstract: In recent years, advances in materials engineering based on adaptive electronics have found a new paradigm to optimize drawbacks in signal processing. A two-layer MnO/ZnO:Zn heterostructure envisioned for frequency adaptive electronic signal processing is synthesized by sputtering, where the use of internal states allows reconfigurability to obtain new operating modes at different frequency input signals. X-ray diffraction (XRD) analysis is performed on each layer, revealing a cubic structure for MnO and a hexagonal structure for ZnO:Zn with preferential growth in [111] and [002] directions, respectively. Scanning electron microscope (SEM) micrographs show that the surface of both materials is homogeneous and smooth. The thickness for each layer is determined to be approximately 106.3 nm for MnO, 119.3 nm for ZnO:Zn and 224.1 nm for the MnO/ZnO:Zn structure. An electrical characterisation with an oscilloscope and signal generator was carried out to obtain the time-response signals and current-voltage (I-V) curves, where no degradation is detected when changing frequencies within the range of 100 Hz to 1 MHz. An equivalent circuit is proposed to explain the effects in the interface. Measurements of switching speeds from high resistance state (HRS) to low resistance state (LRS) at approximately 17 ns, highlight the device's rapid adaptability, and an estimated switching ratio of approximately 2×10^4 indicates its efficiency as a memristive component. Finally, the MnO/ZnO:Zn heterojunction delivers states that are stable, repeatable, and reproducible, demonstrating how the interaction of the materials can be utilised in adaptive device applications by applying frequencies and internal states to create new and innovative design schematics, thus reducing the number of components/connections in a system for future sustainable electronics.

Keywords: MnO; ZnO:Zn; memristor; I–V curves; adaptive electronics; sustainable electronics

1. Introduction

Different approaches of signal processing are being developed largely driven by Moore's law [1,2]. One of these approaches is through adaptive electronics. An adaptive device can be defined as an electronic structure designed to incorporate internal mechanisms (states) capable of reconfiguration, enabling new operating modes. The structure's reaction to an external stimulus (such as a change in frequency) will self-adjust the parameters of those properties to carry out certain electronic operations [3–5].Therefore, frequency-adaptive electronic signal processing devices can be considered as a feasible solution for

Citation: Neri-Espinoza, K.A.; Andraca-Adame, J.A.; Domínguez-Crespo, M.A.; Gutiérrez-Galicia, F.; Baca-Arroyo, R.; Dorantes-Rosales, H.J.; Peña-Sierra, R. MnO/ZnO:Zn Thin-Film Frequency Adaptive Heterostructure for Future Sustainable Memristive Systems. *Nanomaterials* 2024, 14, 659. https:// doi.org/10.3390/nano14080659

Academic Editors: Jose Maria De Teresa, Ricardo Lopez Anton and Sion Federico Olive Méndez

Received: 17 March 2024 Revised: 4 April 2024 Accepted: 8 April 2024 Published: 10 April 2024



Copyright: © 2024 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). the future of high-speed and low-power electronic devices in which dynamic self-adjusting parameters can be reconfigured by manipulating its properties. Examples of adaptive behaviour can include the use of polarization (spintronics), oxide attributes (multiferroics, piezoelectricity, strain), modifications in dimensions (thickness and area), and nonlinear conduction (memristors) [6–11]. Memristive behaviour (memristor is a combination of the words "memory" and "resistor") [12] are typically found on metal oxides where the switching of different states can be manipulated with electronic transport mechanisms such as migration of oxygen vacancies, conduction through filament paths, and capacitive-inductive effects [13–17]. A main characteristic of an ideal memristor is a zero-crossing pinched current-voltage (I–V) hysteresis curve (I = 0 and V = 0). Several previous works have found that the interaction of heterojunctions of transition metal oxides (TMOs) can create non-zero-crossing points in the I–V curve [10,16,18,19]. This phenomenon can occur for various reasons [10,16] such as inductive and capacitive effects, indicating a need for expanding the memristive theory to assign more coupled effects and new applications.

A number of TMO structures involving ZnO and MnO_x (such as MnO_x/HfO_x [20], Pt/MnO_x/Pt [21], Pt/ZnO/Pt [22]) have reported resistive switching characteristics.

Table 1 presents a brief comparison of memristive devices of different materials, showing key attributes such as thickness, conduction mechanisms, I-V curve types, threshold voltages, switching ratios, and switching speeds. The threshold voltage and switching ratio serve as critical indicators of the energy requirements and data distinction capabilities of these devices, while the switching speed focuses on the performance in high-speed applications. Commercial memristors typically have switching speeds in the range of 50 ns -100μ s [23]. A more profound study of switching mechanisms is needed to fully understand how speed affects application performance. As can be seen from Table 1 and other comparison tables reported [11,24–27], most structures consist of three or more layers/interfaces. This reflects greater complexity for the synthesis process and likewise, the transport mechanisms become more intricate to study. The proposed bilayer structure reduces the memristive response to one interface and two materials with their oxides. Due to the simplicity of the structure, it is possible to propose an equivalent circuit to explore how the interface could be translated to already known electronic components, with the purpose of understanding the internal switching adaptive mechanisms through frequency variation. In this work, switching is proposed to occur with the variation of frequency in order to control the states.

These behaviours and parameters are of great interest to the development of neuromorphic materials as well as new applications for sustainable electronics [28–31], as different transport mechanisms in the interface can help reduce the number of elements in a structure, making it efficient, reconfigurable, responsive, and low power where components can be passive (resistors, inductors, capacitors) or active (transistors, diodes).

In this paper, a simple MnO/ZnO:Zn bilayer thin-film heterostructure is synthesized by the sputtering technique to improve electronic signal processing as a frequency adaptive memristive system. The ZnO has a direct wide bandgap of approximately 3.3 eV, and its most common potential applications are for laser diodes, light-emitting diodes (LEDs) [32], and transparent thin-film transistors (TTFT). Furthermore, Zn-doped ZnO (ZnO:Zn) can be used as a thin-film to design structures to drive the electrical responses using transport and interface phenomena [6,13,15,26]. The Mn and its oxides continue to be an inorganic material of technological importance for environmental remediation, electrochemical capacitors [33–35] as well as metal oxide-based RRAM devices due to the defects, vacancies and oxidation propensity of MnO_x [36,37]. Many of the reported memristive systems are thin-films prepared by different methods such as pulsed laser deposition (PLD), chemical vapour deposition (CVD), and electrochemical and magnetron sputtering deposition. The sputtering offers repeatable, reproducible, scalable, uniform, and high-quality films. These properties are needed to form stable heterostructures/heterojunctions, and this work considers previously determined experimental conditions [38,39].

Materials	Thickness of	Conduction	I–V Curve	Threshold	Switching	Switching	Ref.
	Structure	Mechanism	Type	Voltage (V)	Ratio	Speed (ns)	
$Pt/Ta_2O_{5-x}/TaO_{2-x}/Pt$	~110 nm	Oxygen vacancies	Zero crossing	1	>10	10	[40]
Ag/MnO _x /Pt	~282 nm	Ag filament or by oxygen vacancies	Zero crossing	0.95	$\sim 3.2 \times 10^3$	-	[20]
Ag/HfOy/Pt	~282 nm	Bipolar resistive switching	Zero crossing	0.45	$8.21 imes 10^4$	-	[20]
Ag/MnO _x /HfO _y /Pt	~282 nm	Bipolar resistive switching	Zero crossing	0.65	$6.91 imes 10^5$	-	[20]
Pt/MnO _x /Pt	~250 nm	Ohmic conduction	Non-zero crossing	12	>10 ³	100	[21]
Pt/MnOx/Al	~250 nm	Ohmic conduction	Non-zero crossing	0.3	>10 ³	100	[21]
Ag-ZnO/ZnSnO ₃ -Ag	ZnO NW's (100 nm diameter, 0.5 mm length)	Bipolar resistive switching	Non-zero crossing	1.7	$5.8 imes 10^2$	-	[41]
Pt/ZnO/Pt	~220 μm 100 nm for ZnO	Bipolar resistive switching Filament	Zero crossing	3.3	10 ³ -10 ⁴	-	[22]
MnO/ZnO:Zn	~200 nm	Bipolar resistive switching Filament	Non-zero crossing (f > 100 kHz)	0.44	$\sim 2.11 \times 10^4$	~17	This work

Table 1. Comparison of different materials memristive devices and their reported characteristics.

For the MnO/ZnO:Zn heterostructure of this project, morphological and structural characterisations were carried out by X-ray diffraction (XRD), scanning electron microscopy (SEM), and energy dispersive X-ray spectroscopy (EDS), and were discussed in terms of the electrical performance. The electrical response of the films is studied in the frequency range of 100 Hz to 1 MHz with a digital oscilloscope and function generator. The adaptability of the system through different frequencies and the combination of the proposed metal oxides were analysed in this manuscript to determine potential applications as a frequency-adaptive structure for future sustainable memristive electronic systems.

2. Materials and Methods

The synthesis is crucial to obtain the desired characteristics of the memristive system. For this reason, a detailed explanation of the substrate cleaning procedure, as well as the deposition by sputtering, is provided below.

2.1. Substrate Cleaning Procedure

To remove contaminants on the surface that can lead to defects in the thin-film, affecting its properties, the cleaning of the glass substrate before the deposition is a critical step to ensure the quality and performance of the heterostructure. The cleaning process (as seen in Figure 1) typically involves sonication of the substrate in each reagent, followed by drying it with nitrogen.

This process ensures that the glass substrate is free from organic and inorganic residues, fingerprints, dust particles, and other contaminants that could affect the adhesion and uniformity of the thin-films.



Figure 1. Substrate cleaning process before sputtering deposition.

2.2. Thin-Film Deposition by Sputtering

The Mn and ZnO:Zn samples were synthesized using a physical vapor deposition (PVD) sputtering system from Kurt J. Lesker (Jefferson Hills, PA, USA) with a configuration of two sputter gun sources, DC and RF. The vacuum chamber is evacuated by a mechanical pump for 2 h and later by a turbomolecular pump for 5 min to achieve a pressure of 2.5 mTorr. After that, ultra-high purity (99.999%) Argon (Ar) gas was introduced in the chamber. The targets used are 2" in diameter and 0.256" in thickness; Mn of 99.99%, ZnO of 99.99% and Zn of 99.999% purity. The deposition process was carried out at room temperature and in different stages to guarantee the desires thickness (100 nm) of each film.

In the first stage, the Mn target was used with DC Sputtering source at 30 W and 5 SCCM (Standard Cubic Centimeters per Minute) of Ar with a working pressure of 3.5 mTorr for 90 min.

The next step considers a ZnO:Zn film co-deposition using a RF/DC configuration. The applied power was 125 W for ZnO (RF source) and 5 W for Zn (DC source) with a working pressure of 5 mTorr, Ar flow of 10 SCCM, and a deposition time of 25 min. These conditions have been optimised [39] and offer interesting electrical responses for adaptive devices. Both stages were carried out several times to ensure repeatability and reproducibility. Each set of samples were studied separately and are labelled as MnGl and ZnGl (Gl meaning "on glass"). Table 2 presents the summarized deposition conditions for each layer.

Sample	Sputtering Target	Power Source	Ar Atmosphere	Working Pressure
MnGl	Mn, 99.9% purity	DC, 30 W	5 SCCM	3.5 mTorr
ZnGl -	ZnO, 99.99% purity	RF, 125 W	10 SCCM	5 mTorr
	Zn, 99.999% purity	DC, 5 W	10 SCCM	5 mTorr

Table 2. Parameters for thin-film deposition.

In the final stage, to obtain the bilayer heterostructure, a conventional deposition with a stainless-steel mask was employed. In this process, a grid of circular geometries was used to define the areas of each oxide layer during the deposition (Figure 2).

2.3. Characterisations

A profilometer (KLA-TENCOR) was used to corroborate the average thickness of the films.

XRD was performed to evaluate the structural characteristics of the samples synthesized by sputtering. X-ray diffraction patterns (XRDP) were obtained with a PANalytical X'Pert Pro diffractometer (radiation CuK α , λ = 0.15418 nm) in the range of 30–60° with a step size of 0.04° in 2 Theta-Omega (powder) configuration.



Figure 2. (a) Photograph of complete MnO/ZnO heterostructure, (b) cross-sectional diagram of structure, indicating thickness of as-prepared films, (c) area of deposition showing stainless-steel mask to define each material.

The incident optics used were with 1/8 divergent slit, mirror (parallel beam), and 10 mm of mask. A Pixcell ultrafast detector was used with 256 channels to obtain the pattern. The voltage at 45 kV and current at 40 mA were used for the X-ray tube power.

An estimation of the crystallite size for each sample was caried out using the Debye–Scherrer equation (Equation (1)):

$$D = \frac{k\lambda}{\beta cos\theta} \tag{1}$$

D indicates the crystallite size in nm, λ is 0.15418 nm from the CuK_{α} probe of the diffractometer and β is the full-width at half maximum (FWHM) of the peak from XRDP with instrumental correction due to the measurements. HighScore Plus software (version 3.0e) from PANalytical (Malvern, UK) was used to calculated *D*.

The strain (ε) of the deposited film was calculated by (Equation (2)):

$$\epsilon = \frac{d - d_0}{d_0} \times 100 \tag{2}$$

where d_0 is the theoretical interplanar distance for each peak, and d is the interplanar distance measured from XRDP.

Scanning electron microscopy (SEM) micrographs of the surface and cross-sections of the samples were obtained with a JEOL JSM-6701F (Tokyo, Japan). An energy dispersive X-ray spectroscopy (EDS) attached to the SEM was used to obtain a semi-quantitative analysis of the elements present in each layer.

For the electrical response of the as-prepared heterostructures, I–V (Current-Voltage) curves were acquired and analysed at different frequencies with a Keysight EDUX1002G oscilloscope (Santa Rosa, CA, USA). A function generator integrated into the oscilloscope was employed to produce the sinusoidal signal to emulate transient polarization at a frequency range of 100 Hz to 1 MHz with voltage from -4 V to 4 V corresponding to the low-level injection.

Figure 3a shows the electrical diagram used to measure the MnO/ZnO:Zn heterostructure. A sinusoidal signal was connected in series with a 1 k Ω load resistor designated as R. The voltage signal across the heterostructure was measured directly as CHX, and the equivalent current was monitored by determining the voltage across the load resistor as CHY. The MnO/ZnO:Zn structure acts as a device under test (DUT) in which we know the input and output, and the inside can be modelled with an equivalent circuit in Figure 3b.



Figure 3. (a) Electrical diagram proposed to evaluate MnO/ZnO:Zn heterostructure. CHX and CHY are channels of oscilloscope. (b) Heterostructure is a DUT where, with analysis of signals obtained with oscilloscope, adaptive behaviour dependant of frequency can be related to an analogy of a circuit.

3. Results and Discussion

3.1. Average Thickness of the Films

The PVD sputtering technique allows for fine control of the thickness in the synthesis process. With the purpose of corroborating the measurements made by the equipment, a profilometer is used in each set of samples using a step made with Kapton[®] tape before each deposition.

The thickness average was found to be 107.1 \pm 9.8 nm for Mn and 116.9 \pm 8.4 nm for ZnO:Zn under the sputtering conditions described above. These results are consistent with the information that the sputtering thickness monitor (Inficon SQM-160, Bad Ragaz, Switzerland) exhibits at the end of the synthesis.

3.2. XRD

The XRDP of the MnGl and ZnGl films are shown in Figure 4. The MnGl diffraction pattern shows two peaks: the peak at 34.448° corresponds to MnO cubic (111) phase according to the ICDD #98-065-7311 crystallographic chart. The second peak was observed at 42.378°, which is related to the cubic (101) Mn phase (ICDD #00-017-0910).



Figure 4. Diffraction patterns for MnGl and ZnGl.

From this characterisation, two main statements can be established: (1) MnO films grow with a preferential orientation of the crystals at (111); and (2) it is possible to observe a minimal quantity of metallic Mn indicating that, during the sputtering process, the deposited Mn was not fully oxidised and implies the presence of Mn as conglomerates, and it can be described as a MnO:Mn film at the defined synthesis conditions.

The XRDP for the ZnGl film reveals only one peak at 34.133° with a high preferential orientation, corresponding to the plane (002) of ZnO, according with the ICDD #00-036-1451 chart. Structural parameters were calculated using Equations (1) and (2). The results are presented in Table 3.

Table 3. Crystallite size (*D*), strain (ε), 2 θ (measured θ_m and reference, θ_r) and 2 θ displacement ($\Delta \theta$).

Plane	Phase	2θ _m (°)	2θ _r (°)	Δθ	<i>D</i> (nm)	ε (%)
(111)	MnO	34.448	34.446	0.002	10.3	$-80 imes 10^{-6}$
(002)	ZnO	34.133	34.422	-0.289	16.14	-0.77

In a sputtering and co-sputtering process, the deposition of the film is affected by parameters such as pressure, power, and gas flux, which can provoke stress and defects, altering the stability of the lattice, more so, in the case of the ZnO:Zn. To assess the stress in the as-obtained films, Equation (2) was used. The strain (ε) results indicate that there are tensile stresses in the perpendicular direction to the (002) plane of ZnO and compression in the parallel direction to the plane of the samples. This deformation is associated to interstitial Zn (Zn_i), in which the atom of Zn has a radius of 137 pm and is introduced to the ZnO lattice in the co-sputtering process [42–44]. Zn_i generates an increase in the interplanar distance, which produces defects, stress and strain in the lattice. This inclusion can be linked to an increase in electrical conductivity as the film can be electrically measured (Appendix A). Pure ZnO films display dielectric behaviour whereas the ZnO:Zn system can present an important resistivity decrease [26,45–47].

The MnO films presents almost no strain and is conforming to the glass substrate.

Conditions for bilayer thin-films growth of semiconductors (in this case ZnO:Zn on top of MnO) requires that both materials have a close interplanar distance as to avoid generating interfacial defects. For this reason, the parameter $\Delta d/d$ between top and bottom layers were calculated as follows [48]:

$$\frac{\Delta d}{d} = \frac{top \ material - bottom \ material}{bottom \ material} \times 100 \tag{3}$$

In this equation, d is the interplanar distance from the diffraction patterns for MnO (bottom) and ZnO:Zn (top) respectively. The mismatch is presented on Table 4.

Plane	Layer	d (Å)	$\Delta d/d_{\rm MnO}$ (%)
(111)	MnO	2.601	-
(002)	ZnO:Zn	2.623	0.846

Table 4. Parameters of interplanar distance (d) for MnO (bottom) and ZnO:Zn (top) films.

Table 4 displays the differences involving the semiconductor films deposited by sputtering. The $\Delta d/d_{MnO}$ percentage of the synthesized heterostructure is 0.846%. The relation $\Delta d/d$ must be less than 1% to assure a good coupling between the lattices of the materials and to reduce the probability of defects in the interface [48]. The proposed MnO/ZnO:Zn heterostructure meets the requirement for the bilayer and, as a consequence, is a good candidate for stable memristive systems.

3.3. SEM Micrographs, EDS Analysis, and Substrate Temperature Model

For a morphological and thickness analysis of the samples, SEM micrographs were obtained at $\times 10,000$ and 5 kV for the surface analysis and at $\times 20,000$ and 10 kV for the cross-section images of both the MnO (MnGl) and ZnO:Zn (ZnGl) layers. Additionally, images were taken at $\times 50,000$ and 10 kV for the MnO/ZnO:Zn structure. Figure 5 shows the surface of the samples in Figure 5a, Figure 5c, and Figure 5e respectively. The Mn deposition on glass is uniform and almost no defects are observed. The MnO film exhibits a characteristic mirror-like finish on glass, and upon application of the top ZnO:Zn film, no further oxidation is detected in the original film, which functions as a passivation layer [49]. Figure 5c shows the ZnO:Zn on glass where a labyrinth pattern can be detected [15]. The layer is transparent as already known in ZnO films, only with a certain tinted blue hue for the ZnO:Zn.



Figure 5. (a) SEM micrograph of surface of MnO (MnGl) at $\times 10,000$, (b) cross-sectional image of MnO at $\times 20,000$, (c) micrograph of surface of ZnO:Zn (ZnGl), (d) cross-sectional image of ZnO:Zn at $\times 20,000$, (e) micrograph of surface of structure MnO/ZnO:Zn at $\times 50,000$, (f) cross-sectional image of structure MnO/ZnO:Zn at $\times 50,000$, (g) EDS analysis of MnGl, (h) EDS analysis of ZnGl.

In Figure 5e, the surface of the MnO/ZnO:Zn also shows a homogeneous and smooth surface where the ZnO:Zn pattern prevails as is the top layer of the structure. A homogeneous surface ensures consistent electrical properties across the film, and the smoothness minimizes defect sites and irregularities that could lead to unpredictable switching behaviour or degrade the device response over time.

For the film thickness by SEM, Figure 5b,d,f show MnO, ZnO:Zn, and the final heterostructure of MnO/ZnO:Zn, respectively. The average thickness is determined by six measurements of each layer, resulting in 106.3 \pm 10.8 nm for MnO, 119.3 \pm 6.5 nm for ZnO:Zn, and 224.7 \pm 10.1 nm for the final MnO/ZnO:Zn structure. These results closely align with those obtained by the profilometer for each layer, thereby corroborating the information provided by both the profilometer and the sputtering thickness monitor. Figure 5g,h present the EDS analysis of MnO and ZnO:Zn, respectively, showing that the materials of each film are present as the main elements, with no other atoms found aside from C.

By examining the morphological characteristics of the MnO/ZnO:Zn heterostructure and considering the room-temperature deposition process, we have established a substrate temperature model. Following the method of Khelfaoui and Aida [50], we employ a 1D heat equation model (Equation (4)) to calculate the surface temperature of the Mn and ZnO:Zn films during sputtering. This model allows us to estimate the films' surface temperatures throughout the sputtering process, aiding in corroborating the low-thermal-impact assumption associated with room-temperature sputtering and deepening our comprehension of how temperature influences the deposition and, subsequently, the film's final properties.

$$\frac{\partial T}{\partial t} = \frac{k_{gl}}{C_{gl} \cdot \rho_{gl}} \frac{\partial^2 T}{\partial x^2} \tag{4}$$

where k_{gl} is the glass substrate thermal conductivity at 0.0014 $\frac{W}{cm\cdot K}$, C_{gl} specific heat of the glass at 0.75 $\frac{J}{g\cdot K}$, and ρ_{gl} is the density of glass at 2.5 $\frac{g}{cm^3}$. They indicated that the temperature mostly depends on the substrate material thermal conductivity and thickness [50]. For the 1 mm-thick glass substrate used, the following assumptions are considered for the model:

- There is no heating source for the substrate/substrate holder, so the initial temperature (T_0) is room temperature (fixed at 300 K).
- The energy flux from the targets and subsequently generated plasma is the heating source for the glass substrate and the temperatures are considered equal in the substrate for the growing process.
- The boundary conditions are:

$$T(x,0) = T_0 \tag{5}$$

$$T(0,t) = T_0 \tag{6}$$

$$-\frac{dT(x,t)}{dx}\Big|_{x} = Pd \tag{7}$$

where Pd is the power density of each target. While there are numerous interactions in the sputtering process (including sputtered atoms, Ar atoms, photons, etc.), we primarily consider the energy flux is mainly influenced by the power conditions of each target from the DC and RF sources. The effective area of the target is associated with the toroidal electromagnetic plasma generated during deposition. For our 2" (approximately 5 cm) targets, a radius of 2 cm (effective radius— r_{ef}) is utilized for the power density calculations provided in Table 5. For the co-sputtering process, the power densities were summed, although the 5 W contribution of Zn is minimal compared to the ZnO power. Figure 6 presents the results of the solved 1D heat equation as well as the graphical model illustrating the assumptions, where *x* represents the thickness of the substrate.

Target	Power (W)	Power Density, Pd (W/cm ²)
Mn	30	2.4
ZnO	125	9.94
Zn	5	0.4

Table 5. Power density of each target used in MnO/ZnO:Zn heterostructure.



Figure 6. Solution of 1D heat equation for glass substrate for Mn and ZnO:Zn deposition. Stabilization time of deposition is around 500 s according to equation. Inset shows graphical model used in assumptions and effective area of a target.

Based on the XRD results and with this model, it can be concluded that the temperatures of the substrate during the sputtering process do not exceed 320 K (47 °C), and the crystallinity of the samples indicates that, under the power conditions presented in this paper, the growth film does not exhibit significant defects or stress. Furthermore, SEM corroborates this observation, as the samples shown are homogeneous, and almost no rugosity is visible on the surface.

3.4. Frequency Adaptive Signal Processing

To investigate the adaptive behaviour of the MnO/ZnO:Zn, a bilayer structure was produced with the two-stage synthesis procedure described previously.

The interface operates under a dynamical polarization (time response), exhibiting both resistive and reactive (capacitive and inductive) impedance in the space-charge (SC) region. Therefore, to assess the technological capabilities of the MnO/ZnO:Zn heterostructure, the SC region of the heterojunction is analysed as a transfer function, defined as the ratio between the output and input signals.

Under the measurement technique shown in Figure 3, the dynamic behaviour of the MnO/ZnO:Zn structure can represent the correlation between the transfer function and the corresponding I–V characteristics to reveal internal states under specific operating conditions (in this case, changes in frequency).

The transient activation of states provides a qualitative understanding of the transport mechanisms involved in operating the MnO/ZnO:Zn heterojunction. The input consists of a sinusoidal signal of 4 V for each cycle, representing the condition for reproducible and repeatable states. At 4.8 V, the potential barrier is breached, resulting in a permanent loss of the rectifying behaviour.

The time-response signals, I–V curves, and equivalent circuit with the proposed contribution of each element are illustrated in Figure 7. The time is indicated as arbitrary units (a.u.) as the oscilloscope averages thousands of signals in each period. A time/div is



displayed in each frequency to denote the equivalent period for each grid division on the time axis. It is important to note that the higher the frequency, the shorter the time, as there is an inverse relation.

Figure 7. States of heterostructure where time response, I–V curve, and equivalent circuit are shown for each frequency (external stimulus). CHX and CHY are visible in time-response graph, each having a different scale given attenuation of output signal (CHY). I–V curves reveal evolution of space-charge region at each frequency. Analogy of the circuit is also presented, where simulation for a 1N4007 diode, L = 27 uH, C = 100 pF and Rload = 1 k Ω shows a similar output signal to ones of heterostructure at those frequencies. States are stable and can be achieved repeatedly under a signal of 4 V or less in the input.
An analysis of the performance at different test frequencies, ranging from 100 Hz to 1 MHz, follows. At lower frequencies (100 Hz to 10 kHz), a barrier forms at the interface of MnO/ZnO:Zn, causing the heterojunction to behave as a diode (half wave rectifier). However, at higher frequencies (100 kHz and 1 MHz), the rectifying behaviour changes due to the frequency increase, leading to a transformation of the signal. This change is reflected in the space charge region, which increases as the frequency rises. The hysteresis of the I–V curves is directly related to this alteration. A detailed explanation of the behaviour at each frequency is provided for better understanding of the frequency adaptive signal processing of the device.

At 100 Hz, a rectifying and resistive switching state is observed, with the threshold voltage of the device measured at 440 mV (sinusoidal input). This indicates the onset of diode response, which remains consistent across all frequencies. A filament conduction is presumed at the interface. The presence of filament conduction at the interface is presumed, as evidenced by the time response signal of forward bias rectification and the I–V curve. The rectification originates from the interface between the MnO and ZnO:Zn layers, where a certain number of electrons and holes have flowed, generating the electrical field of the space charge region. Consequently, this resistive switching state can be attributed to space-charge limited currents (SCLC), characterized by charge trapping, leading to a transition from a high-resistance state (HRS) to a low-resistance state (LRS) under forward-bias conditions. This transition corresponds to bipolar resistive switching. From 100 Hz to almost 100 kHz, the signal behaviour resembles that of a rectification-only state.

For 100 kHz, the capacitive rectifying state expands from -4 V to 4 V, indicating that the velocity of injected carriers is lower than the velocity of charge trapping. This extension of the state encompasses the reverse bias region (negative cycle), manifesting as a broadening in the I–V curve within the same voltage range. During this period, there is a transient accumulation of electron and hole carriers around the interface, accompanied by additional charge trapping in the space charge (SC) region. As a result of this transient condition, the SC region extends (with a corresponding reduction in the electric field), leading to a random distribution of carriers in the ZnO:Zn region beyond the interface. This distribution may contribute to the slow ionization of defects, thereby inducing a hysteresis phenomenon in the I–V curve.

In 300 kHz, the rectification effect becomes nearly imperceptible, and a crossing is observed in the hysteresis curve. This phenomenon, known as pinched hysteresis, is characteristic of ideal memristors, which exhibit a zero-crossing pinched hysteresis crossing at I = 0 and V = 0 (Table 1). However, in several reported structures, meminductive and memcapacitive effects can occur at interface [51,52]. In the case of the MnO/ZnO:Zn heterojunction, the pinched response is shifted and asymmetric, indicating imperfect memristors with a non-zero crossing I–V hysteresis [10,12,53]. This suggests that the MnO/ZnO:Zn heterojunction should be considered as an extended memristive device.

At 800 kHz and 1 MHz, the time-response signal does not deliver a rectifying behaviour anymore. A greater capacitive response than the one at 300 kHz is present, as evidenced by the delay of the signal in the negative cycle of CHY relative to CHX. When the signal rises (negative to positive), the capacitive contributions are greater than the resistive ones. On the contrary, when the signal falls (positive to negative) the contributions are almost purely resistive. This capacitive response can be attributed to an expansion of the space charge (SC) region, where holes fill more rapidly due to the higher frequency of the state. This phenomenon is also reflected in the broader hysteresis of the I–V curve. The capacitive response has been studied separately in other work for a similar structure [54]. Appendix B, Figure A1 presents the comparison of the V–t and I–V curves of a simulated circuit compared to the MnO/ZnO:Zn heterostructure for further exploration of the equivalent circuit.

To analyse the transient switching characteristics of the memristor, a square signal of ± 4 V is used as a pulsed signal at 500 kHz with the same configuration as before. Figure 8a



illustrates the input signal, while the response of the structure is depicted in Figure 8b and the conductance for the applied pulses is showed in Figure 8c.

Figure 8. Applying a ±4V square signal to MnO/ZnO:Zn structure, we obtain (**a**) input signal with rise and fall signals indicated in red and blue, respectively; (**b**) response of structure as pulses, where the switching speed is measured in oscilloscope and indicated as 17 ± 0.82 ns for HRS to LRS and 439 ± 21.9 ns for LRS to HRS; and (**c**) conductance for applied pulses where switching ratio is calculated as $2.11 \times 10^4 \pm 6.59 \times 10^4$.

Figure 8a depicts the rise/SET and fall/RESET characteristics of the square signal to simulate pulses at 500 kHz. This frequency was chosen due to its features being representative of both 300 and 800 kHz. In Figure 8b, the response signal was used to measure the switching speeds in the oscilloscope using cursors. The determined values were 17 ± 0.82 ns from HRS to LRS and 439 ± 21.9 ns from LRS to HRS. These speed disparities not only emphasize the heterostructure's quick adaptability to changing electrical condi-

tions but also point towards its potential applications where fast switching mechanisms are needed. Using Ohm's law (V = IR), the resistance values (V as the input voltage and I as the relation of the response voltage and the R_{load} of 1 kΩ), were calculated to obtain the conductance of each pulse (conductance is the inverse of resistance and measured in Siemens, $S = \Omega^{-1}$). Lastly, the switching ratio value was estimated as $2.11 \times 10^4 \pm 6.59 \times 10^4$. This value, reflective of the device's ability to differentiate between resistance states, serves as a fundamental parameter for optimizing the material's nanocomposition and configuration to enhance its memristive efficiency. Appendix C presents the power consumption of the device at different frequencies for additional efficiency parameters.

Finally, the heterojunction does not degrade with the changes in frequency and the states remain repeatable over the spectrum of 100 Hz–1 MHz (meaning that, for example, a jump from 1 MHz to 100 Hz, does deliver the same signal seen in each state). Both the external stimulus of the frequency and the stable, repeatable signals of each state, allows us to determine that the MnO/ZnO:Zn heterostructure can be deemed as a first approach to future sustainable frequency-adaptive memristive systems.

4. Conclusions

A simple MnO/ZnO:Zn heterostructure of approximately 200 nm was synthesized by sputtering and was found to have characteristics of extended memristive devices through frequency analysis. Unlike conventional multilayer memristive systems, this heterostructure capitalizes on a single interface of two materials, streamlining the complexity typically associated with such devices. XRD data show a MnO phase with high texture in (111) whereas the ZnO:Zn film is preferential towards (002) and the doped Zn atoms are introduced as interstitial Zn (Zn_i) which enhances the conductive behaviour of the film in comparison to pure ZnO. SEM showcases a uniform and smooth surface across both materials, a critical attribute for ensuring consistent device performance.

Electrical characterisation, using an oscilloscope and function generator in the range of 100 Hz to 1 MHz, revealed a non-zero crossing I–V hysteresis, as well as capacitive effects associated to the interface, thus demonstrating the frequency adaptability of the system. The responses are stable, repeatable, and reproducible as long as the bias voltage does not exceed the ± 4 V limit. The simple structure allows the analysis of an equivalent circuit model with the purpose of understanding the internal switching adaptive mechanisms through frequency. The switching speed from HRS to LRS of 17 \pm 0.82 ns, highlight the heterostructure's potential in fast-switching applications. Furthermore, the switching ratio of 2.11 \times 10⁴ \pm 6.59 \times 10⁴, opens possibilities for optimising the material's composition and structure to enhance this parameter, such as the improved conductance of the ZnO:Zn which can be exploited for future devices in which conductive, transparent, and easy to deposit ZnO films could be of use for future memristive applications.

As the field of frequency-adaptive devices emerges, the unique interaction between MnO and ZnO:Zn oxides has great potential for the development of new applications and technologies to transition from traditional to sustainable electronics. This study illustrates the potential of leveraging simple heterostructures as an option to create new and innovative design schematics with reduced components and complexity, paving the way for the next generation memristive devices.

Author Contributions: Conceptualization, R.B.-A.; formal analysis, K.A.N.-E., R.B.-A., J.A.A.-A. and H.J.D.-R.; investigation, K.A.N.-E.; methodology, K.A.N.-E.; project administration, J.A.A.-A. and R.B.-A.; resources, J.A.A.-A., F.G.-G. and R.P.-S.; supervision, R.P.-S.; writing—original draft, R.B.-A.; writing—review and editing, K.A.N.-E., J.A.A.-A. and M.A.D.-C. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by the Consejo Nacional de Humanidades, Ciencia y Tecnologías (CONAHCyT, México) under grant #2777300.

Data Availability Statement: Data are contained within the article.

Acknowledgments: This work has been possible thanks to the technical support of Miguel Galván Arellano, Adolfo Tavira Fuentes, and technician Norma Iris González García from Centro de Investigación de Estudios Avanzados del Instituto Politécnico Nacional (CINVESTAV-IPN, México).

Conflicts of Interest: The authors declare no conflicts of interest.

Appendix A. Hall Effect Measurement

An electrical characterisation of each layer was made by Hall effect employing the Van der Pauw method using a magnetic field of 0.55 Tesla.

The information from the Hall measurements allows to know the carrier density, mobility, and resistivity of each film. In the ZnO:Zn sample, the Zn incorporation decreases the resistivity and can be measured in comparison to a ZnO film at the same conditions of synthesis [46]. Table A1 indicates the values obtained.

Sample	Туре	Carrier Density (cm ⁻³)	Mobility (cm ² /V-s)	Resistivity (Ω-cm)
MnGl	р	$3.40 imes10^{21}$	0.00762	0.2385
ZnGl	n	$3.00 imes 10^{16}$	9.2182	24.6547

Table A1. Parameters obtained from Hall measurements for MnGl and ZnGl samples.

The difference in semiconductor types for each film can be seen from the results of Table A1. The structure can take advantage of the p-n heterojunction type for a reconfigurable device. For the MnO layer, the main carriers will be the holes (h+) acting as acceptors and for the ZnO:Zn layer, the carriers will be the electrons (e-) acting as donors.

Appendix B. Simulation of Equivalent Circuit

The comparison between the measured MnO/ZnO:Zn structure and the simulated equivalent circuit with the simulation program with integrated circuit emphasis (SPICE) is shown in Figure A1. The V–t and I–V curves are similar, and the main change is the intensity of the signals as the simulated signals show a minor attenuation in voltage and current. This circuit analogy allows us to observe what the behaviour of the interface between MnO and ZnO:Zn may be like with passive and active elements.



Figure A1. Cont.



Figure A1. Cont.



Figure A1. Comparison of V-t and I-V curves of simulated circuit in SPICE versus MnO/ZnO:Zn response.

Appendix C

The power consumption can be calculated as dynamic power consumption (Equation (A1)) given the frequency change at different states:

$$P = CV^2 f \tag{A1}$$

As we have the capacitor (*C*) value from the equivalent circuit as 100 pF, the frequency is our variable and Table A2 shows the power consumption at each frequency.

Frequency	Dynamic Power Consumption	
100 Hz	160 nW	
100 kHz	160 μW	
300 kHz	480 μW	
500 kHz	800 µW	
800 kHz	1.28 mW	
1 MHz	1.6 mW	

Table A2. Dynamic power consumption of MnO/ZnO:Zn structure at different frequencies.

As the frequency rises, so does the power consumption. This is a direct relation of Equation (A1) and can be explained as: the more signal that is supplied to a device at higher frequencies, the input signal is faster and repeated more times than at a lesser frequency, increasing the consumption of energy.

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Article The Effect of Applying UV LED-Cured Varnish to Metalized Printing Elements during Cold Foil Lamination

Igor Majnarić^{1,*}, Marko Morić², Dean Valdec² and Katja Milković³

- ¹ Faculty of Graphic Arts, University of Zagreb, 10000 Zagreb, Croatia
- ² Department of Art Studies, University North, 48000 Koprivnica, Croatia; mmoric@unin.hr (M.M.); devaldec@unin.hr (D.V.)
- ³ Juraj Dobrila University of Pula, Zagrebačka 30, 52100 Pula, Croatia; katja.milkovic@unipu.hr
- Correspondence: igor.majnaric@grf.unizg.hr

Abstract: The coating process involves applying a thin material layer to a surface to engender it with specific desirable properties or enhance its performance. In the production of print media (labels, packaging, printed textiles, and promotional materials), the standard functions of the coating process include visual decoration, which involves the addition of appealing colors, textures, and patterns. A pertinent issue in the printing industry is that at present, the predominant coating process uses printing and coating technologies (gravure, flexo, letterset, letterpress, screen printing, inkjet, and electrophotography) and lamination (i.e., attaching decorative layers of materials, such as films or fabrics). In this paper, we present a new method for testing the efficiency with which different-sized metalized printing elements (using gold foil) may be applied to paper substrates; to do so, we gradually vary the amount UV-cured inkjet varnish (or adhesive) that is applied. To test the effectiveness of this method in producing metallic visual effects, we utilize seven different thicknesses of UV-cured varnish with the aid of modular piezo inkjet heads (KM1024 iLHE-30) and three different printing speeds. Our research shows that to achieve optimal production of cold metalized foil, a 21 μ m layer should be deposited, and the substrate should move at a speed of 0.30 m/s.

Keywords: UV-cured inkjet; metalized foil; varnish thickness; methods of testing metalized effects

1. Introduction

The industrial coating process involves applying a thin layer of material onto a surface to imbue it with specific desirable properties or enhance its performance. Coatings can serve various purposes, depending on the method of application and the type of coating used. Some standard functions of the industrial coating process include protection, decoration, abrasion resistance, adhesion, lubrication, electrical conductivity or insulation, acting as a thermal barrier, chemical resistance, and adding hydrophobic, hydrophilic, antimicrobial, optical, and barrier properties [1].

For industrial decorative purposes, coating materials are often chosen for their ability to provide a pleasing and eye-catching finish. Painting, powder coating, anodizing, electroplating, printing and/or coating technologies, special effects coatings, ceramic and glass decoration, automotive customization, architectural coatings, and laminating and veneering are just some of the forms that the coating process can take [2].

Foil printing methods, in terms of efficiency and efficacy, are currently dominated by UV flexographic and UV lithographic offset printing technologies, the main reason being that they cause prints to dry quickly. Polymer printing involving the controlled production of small printing elements has a great influence on the size and forming limits of printed items in later micro-stamping procedures [3,4].

Citation: Majnarić, I.; Morić, M.; Valdec, D.; Milković, K. The Effect of Applying UV LED-Cured Varnish to Metalized Printing Elements during Cold Foil Lamination. *Coatings* **2024**, *14*, 604. https://doi.org/10.3390/ coatings14050604

Academic Editors: Giorgos Skordaris, Ricardo Lopez Anton, Jose Maria De Teresa and Sion Federico Olive Méndez

Received: 3 March 2024 Revised: 7 May 2024 Accepted: 8 May 2024 Published: 10 May 2024



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2. Theoretical Basis

2.1. Lamination

Laminating processes are commonly used in printing industries including furniture manufacturing, interior design, architecture, and automotive customization. These processes generally involve bonding multiple layers of materials together to create a new composite structure. The layers may be made of different materials, each serving a specific purpose.

In the printing industry, laminating is a process used to apply thin layers of material such as polymer or metal films, fabrics, or other decorative materials—to printed paper and cardboard in order to enhance both their appearance and durability. To complement the lamination process, the entire pre-printed surface (e.g., cardboard packaging and book and magazine covers) is coated to prevent mechanical rubbing during practical use. A typical procedure includes the preparation of the printed substrate (for a reduction in surface tension or the elimination of static electricity), application of an adequate adhesive (UV-cured varnish using a coating unit), adhesion through the application of temperature and pressure (via heated rollers or a flat thermal press), and final finishing (removal of imperfect edges on the web roll or cutting to the final desired dimensions) [5,6].

2.2. Printing of Decorative Metalized Foil

To achieve appealing effects in their marketing and sales work, graphic designers frequently use partial application of metalized foil as a special effect. The most challenging aspect of this is achieved by hot or cold application, wherein multi-layer printing foils are used instead of metallic printing inks. The composition of said metalized foil is complex and usually contains four layers: a polyester carrier layer, an intermediate releasing layer, a metalizing layer, and an adhesive layer (Figure 1).





To perform hot foil application, it is necessary to create a magnesium printing form (cliché) for letterpress printing (in which printing elements are situated higher than unprinted surfaces); said form is then selectively melted by heating from 80 °C to 200 °C, and with significant pressure (10 MPa), the adhesive and printing substrate are combined. The success of the separation and acceptance of the metal layer thus depends on factors such as the structure of the substrate, the thermal coefficient of the printing substrate, the printing speed, the cliché temperature, and the thickness of the printing foil. Typical hot embossing processes (carried out via a flat die press and a hot silicone rubber roller) are shown in Figure 2a,b [8,9].

The cold foil printing process requires specialized multi-color offset printing machines that contain at least two printing units (Figure 3). The first printing unit applies the adhesive (a varnish or pasty ink). At the same time, the second unit brings the metalized foil into contact with the printing substrate (in the gap between the printing and offset cylinders). The full foil printing procedure is carried out on six-color UV offset printing machines, which combine a classic CMYK color printing unit with a unit for the partial or full printing of metallic foil; using this method, metallic effects can be produced with CMYK inks. Due to offset machines' printing speed, the complexity of the printing process is challenging. This is the reason for the limited number of commercially available metalized foils for this printing process. Kurz is the current industry leader in developing and producing metalized foils for the cold transfer process. Kurz now has nine metalized foils that are



applied using lithographic offset techniques (the LIGHT LINE series) and flexo printing (the LUXOR ALUFIN series).

Figure 2. Principles of and tools for hot foil printing: (**a**) vertical hot foil printing machine; (**b**) roll-on hot foil printing machine [10].



Figure 3. Principles of hot foil printing: (a) vertical hot foil printing machine; (b) roll-on hot foil printing machine [8].

The LIGHT LINE series foils create metalized aluminum, holographic, and transparent effects (type KP is intended for narrow webs, type KPO only for UV inks, and type KS for sheet-fed printing machines). The series created for flexo printing, LUXOR ALUFIN, consists of aluminum metalized and transparent foils (type KPW and KPW-OP-KB for narrow webs and aluminum metalized KPW-OP for UV inks only). The aluminum metalized foils KPS, KPS-OF, and KPS-OS are used for flexo sheet-fed printing machines [10–12].

UV-cured varnish (adhesive layer) is placed directly on the printing surface, after which heat and pressure are applied to the metalized foil. The basis of such systems is the piezoelectric inkjet head, which contains a large number of nozzles arranged in rows and columns (Figure 4a). Drops of adhesive (UV-cured varnish) are formed by the activation of the upper electrode, resulting in mechanical distortion of the micro-piezoelectric element. Such action reduces the volume of the inkjet chamber in which the adhesive varnish is stored. This culminates in the release of plenty of droplets of a minimal volume. Depending on the nozzle number, the distance between the printing lines, the speed of head movement, and the number of head passes, it is possible to apply different amounts of UV-cured varnish and thus augment the quality of the coating. The precision of the application and the details executed directly depend on the volume of the generated droplets, which can vary from 2 to 90 pl [13–16].

The development and application of inkjet technologies have been undertaken by numerous world-famous electronics companies (HP, Palo Alto, CA, USA; Kodak, Rochester, NY, USA; Konica Minolta, Chiyoda City, Japan; Kyocera, Kyoto, Japan; Fuji, Tokyo Mid-town, Japan; Ricoh, Tokyo, Japan; Epson, Nagano, Japan; Spectra, Denver, CO, USA), who have produced numerous inkjet machines [13,17]. Some novel piezo inkjet heads currently on the market are the Konica Minolta KM1024i series heads [18]. The built-in heater in these heads enables stable temperature control of highly viscous solvent inks, UV-cured inks, and oil-based inks. These heads have 1024 nozzles (in a high-density structure featuring four lines of 256 nozzles), corresponding to a printing width of 72 mm (Figure 4b). As they

can be operated at a frequency from 27 to 56 kHz, they are ideal inkjet printing heads for high-speed single-pass inkjet printers. Ultimately, their native addressability is 360 npi (90 npi \times 4 lines), which corresponds to a drop size of 30 pl, 13 pl, and 6 pl (with eight greyscale levels) [19].



Figure 4. Construction of an inkjet piezo nozzle for applying UV-cured ink (adhesive): (a) schematic view; (b) KM series head KM1024i [18].

The curing of colorless UV varnish involves a photopolymerization reaction between monomers/oligomers, photoinitiators, and additives. Reactive monomers/oligomers (most often acrylates and less often unsaturated polyester resins) are the basis of UV inkjet varnish formulations and enable the additional polymerization of free radicals. By increasing the functionality of monomers/oligomers, the number of cross-linkers (and thus the density of the polymer film) can be increased. A greater number of cross-linkers in the polymer film results in the formulation of a firmer, less elastic film that is more resistant to solvents, wear, and scratches; however, these films also exhibit reduced adhesion due to shrinking as a result of UV radiation (fixing) [20].

Depending on their intended application, the operability of inkjet heads and machines needs to be tested. Various scientific papers, international standards (ISO, IEC), and national standards (DIN, ASTM, JIS) have examined printing elements and inks [21–29].

Therefore, this paper aims to examine the success of detecting the quality of the metallic surface without using methods based on line width and line darkness measurements. The inkjet printing process requires the fulfillment of two criteria: quality in both the direction of printing (MD = machine direction) and the alignment of the nozzles (CD = cross direction). A module of five inkjet heads of type KM1024iLHE-30 has a factory-declared addressability of 360 dpi (CD), while the addressability in the machine direction (MD) is not declared because it depends on the selected speed of the printing substrate. In addition, the paper featured optimum settings for the application of UV-cured adhesive using the Konica Minolta inkjet head KM1024iLHE-30 and for the successful transfer of the laminated film to the substrate, a fine art board [30].

3. Materials and Methods

A modified contrast–resolution test chart was used for this experiment. Print images had an addressability of 1200 spots per inch, utilizing a screen with 133 lines per inch. The circular patterns of samples were as follows: 0.63 cy/mm (2 circles), 0.81 cy/mm (3 circles), 1.04 cy/mm (4 circles), 1.35 cy/mm (5 circles), 1.74 cy/mm (6 circles), 2.91 cy/mm (7 circles), 3.76 cy/mm (8 circles), 4.85 cy/mm (9 circles), and 6.25 cy/mm (10 circles). The original contrast row of column A to column J was removed, causing the sample to form an achromatic bitmap [19].

The bitmapped form was saved in PDF format using Adobe Illustrator, making it suitable for the raster image process (Hakiri KM IC602). An identical Hakiri KM IC602 controller was used to make the reference print (a high-quality black-and-white image with a resolution of 1200×3600 dpi) alongside an EP machine from the Japanese manufacturer Konica Minolta Accurio Print C3080 with an associated black Simitri powder toner [30].

UPM semigloss double-coated cardboard was used for fine art prints (with SRA3+ format dimensions and a 300 g/m^2 grammage during the printing process) [31].

The experimental samples were printed on an identical printing substrate and a JET Varnish 3DS film varnishing and printing machine, which has 5 inkjet print heads (KM 1024 LHE-30 positioned in the distribution of 3 + 2 heads) and a UV light source module consisting of 2 LED lamps. The first LED UV lamp contains 4 modules with a power of 5 W, while the second LED UV lamp has only 1 module with a power of 12 W. For UV treatment, LED UV lamps emit a wavelength of 395 nm [32].

Six different coatings (from 21 μ m to 58 μ m) were printed using MGI UV inkjet fastdrying varnish. The JETVARNISH 3DS machine features HubManager 2.8.5 software, using which it is possible to directly adjust the varnish applied. Data on the application of LED UV varnish were not obtained directly through measurement but were obtained indirectly (from the data of the manufacturer). The fast-drying glossy varnish JV3DS contains acrylic monomers and polymers, photoinitiators, and various additives. The main ingredient is the polymer diphenyl (2,4,6-trimethyl benzoyl) and phosphine oxide (CH₃)₃C₆H₂COP(O)(C₆H₅)₂) [33].

Alongside the varnish application unit and the LED drying lamp, there is a metalized foil application unit (foils). Murata Gold-type foil was used. The length of the metalized foil was 500 m, meaning a maximum transfer of $32 \text{ cm} \times 45 \text{ cm}$ foil could be achieved. The temperature was controlled in 6 independent zones, with the possibility of regulating the foil temperature from 90 °C to 190 °C (a constant heater temperature of 105 °C was used for the experiment). RIP MGI Juti 3.2 was used to control the application of transparent varnish. In contrast, an AIS scanner with 180 defined check positions was used to manage the position of the varnish channel. The varnish channel was created using the alpha channel generated in Adobe Photoshop CS6 25.7 [34].

For research purposes, nine samples were printed (divided into three experimental wholes). In the first experiment, the quality of varnish acceptance was tested with an Elcometer 480 gloss meter, which was used to assess 12 points on the surface with only printed lacquer, on the printed gold foil, and on the unprinted substrate [35]. The second part of the research consisted of 6 samples in which the thickness of the varnish varied before contact with the foil (21 μ m, 29 μ m, 36 μ m, 43 μ m, 51 μ m, and 58 μ m). In the third part of the research, the printing substrate's movement speed varied (0.300 m/s, 0.240 m/s, and 0.159 m/s), and varnish was consistently applied in a 21 μ m thick layer. After forming the samples for image analysis, the samples were scanned in a CanoScan LiDE 700F scanner (RGB image, 600 dpi, TIFF format) (Canon, Fukushima, Japan). Before image analysis (corresponding to the contrast–resolution test chart), all images were cut in Adobe Photoshop to the same TIFF grayscale format (size 9 × 6 cm with an original resolution of 600 dpi). We used the open-source program ImageJ 1.5.3 with the following macro program to calculate surface coverage.

```
run("HSB Stack");
run("Stack to Images");
selectWindow("Saturation");
close();
selectWindow("Hue");
close();
selectWindow("Brightness");
run("Options...", "iterations = 1 count = 1");
setOption("BlackBackground", false);
```

Based on the detected black pixels, the area of the contrast–resolution test was determined, the average results of which were processed and analyzed using OriginPro 8.5. Figure 5 shows a flow chart of the experiment.



Figure 5. Chronological flow of the experiment.

4. Results and Discussion

To determine the successful acceptance of the metalized foil, it is necessary to perform a preliminary analysis of the substrate and an analysis of the varnish's adhesion. For this purpose, optical reflectance (gloss measurement) was used to create profiles at 12 characteristic positions on the cardboard substrate, the cardboard substrate with varnish, and the cardboard substrate with both varnish and adhered foil. For this purpose, a three-channel gloss meter—which is intended for measuring matt, semi-matt, and glossy surfaces—was used according to the ISO 2813:2014 standard [35]. After measurement with ten replicates (samples), the mean value of each of the 12 positions was calculated. These values are presented in the profile graph in Figure 6.

Observing the profiles, it can be seen that the lowest gloss value was determined for matte-coated cardboard, with an average value of $G_{avg} = 47.8$ GU. On the surface of the cardboard, the measured gloss values varied between the minimum amount of gloss, $G_{min} = 40.1$ GU (position 5), and the maximum amount of gloss, $G_{max} = 53.6$ GU (position 3). This alone resulted in a change of $\Delta G = 13.5$ GU in the gloss value of the paper, which means that the surface is very uneven and has highly varied glossiness (indicating roughness).



Figure 6. Gloss profiles of the surfaces used in the experiment (cardboard, cardboard + varnish, cardboard + varnish + foil).

The thickness of the varnish directly affects the acceptance of the metallic foil. Greater varnish thickness engenders better foil adhesion. Additionally, the uniformity of the varnish is crucial for the homogeneity of the film's adherence. Further analysis shows that the varnish applied in a 21 μ m layer had a higher gloss value than the cardboard substrates. The mean gloss value of the varnished surface was G_{avg} = 75.8 GU, and the values varied between the minimum amount of gloss, G_{min} = 58.4 GU (position 1), and the maximum amount of gloss, G_{max} = 82.0 GU (position 11). Therefore, the change in the gloss value of the varnish amounted to ΔG = 23.6 GU. The varnishing process did not result in a uniform surface, and the inkjet technique using the KM 1024 and LHE-30 heads produced uneven deposits in the overlapping zones of the print heads.

The metalized surface achieved very high gloss values of over 1000 gloss units. However, we observed fluctuations in the degree of metallic luster. The used metallic foil Murata Gold exhibited the highest shine, with an average value of $G_{avg} = 1198.0$ GU. The extremes ranged from a minimum brightness value of $G_{min} = 1137.6$ GU (position 4) to a maximum brightness value of $G_{max} = 1236.7$ GU (position 5). We observed a great change of $\Delta G = 99.1$ GU in the glossiness of the film. Although such a deviation in gloss values is significant, it was not visually perceptible; that said, it still suggests that the adherence of the film was imperfect.

The central aim of the experimental work was to determine how the thickness of UV-cured varnish (adhesive) affects the reproduction accuracy of small printing elements. To obtain the most accurate results, a high-quality BW print was taken as a reference (via electrophotography with a raster output scanner imaging unit) rather than the original digitized image. Figure 7 shows the results of the surface acceptance of metalized printing elements, while Figure 8 shows bitmap images of digitized metalized samples before Image J analysis.

In analyzing the metalized surfaces of the samples (made with seven different thicknesses of varnish application at a constant printing speed machine of 0.300 m/s), we observed that the surface of the accepted metal foil increased with the increase in the thickness of the varnish applied. However, this increase in the surface area was accompanied by a closure of finer circles and a loss of finer details in the image. Compared to the EP reference sample, all metalized elements were of lower quality and showed a visible loss of circular segments. The best impression (i.e., the smallest increase in the printed area achieved) was made with sample S2 ($\Delta A_{ref_21\mu m} = 152.39 \text{ mm}^2$). Sample S7 had the most significant increase in surface area with the thickest varnish application ($\Delta A_{ref_58\mu m} = 1611.625 \text{ mm}^2$). At the same time, rows 5 to 10 (with 5 to 10 circles in the field) were completely closed and therefore presented as a solid color; the varnish pattern on the circular surface completely disappeared and instead formed a homogeneous solid golden tone. The most significant deviation in the surface was thus observed in the samples with the smallest and most significant application of UV-cured varnish; this difference amounts to ΔA_{S2} s₇ = 1459.24 mm².



Figure 7. Results of the resolution test of samples created by varying the application varnish with a JET Varnish 3DS machine: (a) printed area in mm²; (b) deviation between samples and EP reference.



Figure 8. Cont.





Besides the thickness of the varnish coating, a parameter that also affects the quality of inkjet printing is the printing speed. When analyzing the metalized surfaces of samples made with three different varnish application speeds (with a constant application thickness of $21 \,\mu$ m), minimal changes in the acceptance of the metal foil were observed. Figures 9 and 10 shows the results of surface acceptance of metalized printing elements, while Figure 8 shows bitmap images of digitized metalized samples before ImageJ analysis.



Figure 9. Sample resolution test results obtained by varying the printing speed of the JET Varnish 3DS machine: (**a**) printed area in mm²; (**b**) deviation between samples and EP reference.

The analysis of the surfaces of the printed samples created by varying the speed of varnish application shows that the surfaces of sample S2 and sample S9 were almost equal ($\Delta A_{S9-S2} = 0.0768 \text{ mm}^2$). However, the 0.15 m/s increase in speed resulted in a partial loss (not transference) of more minor elements on the print. The largest surface area was achieved at a speed of 0.240 m/s ($A_{S8} = 4.6645 \text{ mm}^2$), representing an increase of $\Delta A_{max} = 255.263 \text{ mm}^2$ from that of the reference print. This led us to conclude that the tested varnish application speed did not significantly affect the printing resolution.



Therefore, it can be established that the gain and loss of information upon resolution testing are affected more by the increase in varnish applied than by changes in application speed.

Figure 10. Bitmap images of metalized elements after cold foil transfer: (**a**) EP reference; (**b**) layer generate with speed 0.300 m/s; (**c**) layer generate with speed 0.240 m/s; (**d**) layer generate with speed 0.159 m/s.

5. Conclusions

The modified method of analyzing prints using inkjet technology presented herein achieved more realistic results than previous methods because circular image elements do not differentiate between machine direction (MD) and cross direction (CD). However, the cold foil process carried out with the Konica Minolta inkjet head KM1024iLHE-30 generated metalized samples without achieving high-quality reproduction (i.e., from 4.85 cy/mm to 6.25 cy/mm) via small printing elements.

Due to the uneven surface treatment of the factory-produced semigloss-coated cardboard, the application of the UV varnish was not uniform (upon gloss detection) and, therefore, neither was the application of metallic foil. With increased varnish application, each metalized print exhibited an increased surface area. However, with more extreme varnish applications, more and more of the finer parts of the reproduced images were lost. Regulating the speed with which UV varnish was deposited did significantly affect the transfer of the metalizing foil, and a higher speed did not produce good results.

Upon experimentally increasing the thickness of the varnish coating, the printed surface increased by 29.43%, and a minimum area of 4.66% was achieved by varying the speed. Using the JET Varnish 3DS printing system (MGI Digital Technology, Fresnes, France) with KM 1024 iLHE-30 heads and acrylic fast-curing glossy varnish (JV3DS varnish), we attained optimal results with a coating thickness of 21 μ m and a printing speed of 0.300 m/s.

Author Contributions: Conceptualization, I.M. and M.M.; methodology, M.M.; software, K.M.; validation, D.V., I.M. and K.M.; formal analysis, K.M.; investigation, M.M.; resources, D.V.; data curation, D.V.; writing—original draft preparation, I.M.; writing—review and editing, I.M and M.M.; visualization, K.M.; supervision, I.M. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: This paper does not contain data supporting the reported results.

Conflicts of Interest: The authors declare no conflicts of interest.

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Article



A Strategy of Candle Soot-Based Photothermal Icephobic Superhydrophobic Surface

Chenlu Qian⁺, Lu Wang⁺, Qiang Li^{*} and Xuemei Chen^{*}

MIIT Key Laboratory of Thermal Control of Electronic Equipment, School of Energy and Power Engineering, Nanjing University of Science and Technology, Nanjing 210094, China; qianchenlu359@163.com (C.Q.); wanglullaby@163.com (L.W.)

* Correspondence: liqiang@njust.edu.cn (Q.L.); xuemeichen@njust.edu.cn (X.C.)

⁺ These authors contributed equally to this work.

Abstract: Anti-icing/de-icing is of fundamental importance in practical applications such as power transmission, wind turbines, and aerofoils. Despite recent efforts in developing engineering surfaces to delay ice accumulation or reduce ice adhesion, it remains challenging to design robust photothermal icephobic surfaces in a durable, low-cost, easy-fabrication manner. Here, we report an intelligent candle soot-based photothermal surface (PDMS/CS60@PDMS/Al) that can utilize sunlight illumination to achieve the multi-abilities of anti-icing, de-icing, and self-cleaning. Our method lies in the construction of hierarchical micro/nanostructures by depositing photothermal candle soot nanoparticles, which endow the surface with superior superhydrophobicity and excellent photothermal performance. The underlying mechanism is exploited by establishing the heat transfer model between the droplets and the cooled surface. We believe that the smart PDMS/CS60@PDMS/Al developed in this work could provide a feasible strategy to design intelligent engineering surfaces for enhanced anti-icing/de-icing.

Keywords: candle soot; photothermal; icephobic; superhydrophobic; sun illumination

1. Introduction

Ice formation and accumulation is a ubiquitous and unavoidable phenomenon that exists in numerous engineering fields, including power transmission, refrigeration, wind turbines, and aerofoils [1–3]. For instance, the occurrence of ice accretion on wind turbines in harsh environments can lead to a loss of up to 50% of the annual production [4]. Hence, it is urgent to develop effective and reliable anti-icing/de-icing strategies. The traditional strategies to mitigate ice accumulation after freezing include electrothermal de-icing [5], chemical de-icing [6], and mechanical de-icing [7]. Despite the fact that ice on cold surfaces can be removed by Joule heating or mechanical vibrations, these methods are all energy-consuming, inefficient, and eco-unfriendly [8,9].

Recent advances in micro/nanotechnology and surface functionality have spurred the development of intelligent engineering surfaces to prevent ice nucleation, delay ice accumulation, and reduce ice adhesion after freezing. Manna et al. [10] summarize the various reports published over the years that have elaborated on the distinctive importance of both chemistry and topography in imparting and modulating various bio-inspired wettability. Some strategies have been proposed to design the slippery liquid-infused porous surface (SLIPS), targeting reducing ice adhesion once freezing happens [11,12]. The SLIPS is created by infiltrating the micro/nanostructured porous structures with a lubricating fluid. The lubricant on the SLIPS is immiscible in most aqueous solutions and effectively blocks the direct contact between the droplet and the surface. When ice forms on the SLIPS, ice adhesion is extremely low due to the existence of the lubricant layer. However, the SLIPS would lose anti-icing/de-icing properties once the lubricant layer was depleted [13,14].

Citation: Qian, C.; Wang, L.; Li, Q.; Chen, X. A Strategy of Candle Soot-Based Photothermal Icephobic Superhydrophobic Surface. *Coatings* 2024, 14, 612. https://doi.org/ 10.3390/coatings14050612

Academic Editor: Ludmila B. Boinovich

Received: 9 April 2024 Revised: 9 May 2024 Accepted: 10 May 2024 Published: 12 May 2024



Copyright: © 2024 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). Therefore, the SLIPS may not be durable for practical applications. Some other strategies have been adopted to construct micro/nanostructures on superhydrophobic surfaces, aiming to delay ice nucleation. It is reported that the superhydrophobic surface with hierarchical micro/nanostructures can delay ice nucleation and decrease ice accumulation by reducing the contact area between droplets and the surface [15–17]. Unfortunately, ice can simply form on the superhydrophobic surface under subzero-degree conditions. Once ice interlocks with the micro/nanostructures, the superhydrophobic surface loses its workability, leading to an increased ice adhesion force [18,19]. It is well known that the utilization of photothermal materials such as plasmonic particles, magnetic particles, and carbon nanomaterials to construct functional surfaces that can generate heat via light illumination [20,21]. Combined with superhydrophobicity, the photothermal surface can prevent ice nucleation, delay ice accumulation, and even melt accumulated ice layers [22,23]. This endows the photothermal surface with robust abilities for both anti-icing and de-icing in extreme environments [24–27]. Miao et al. [28] reported a facile strategy of employing ice crystals to construct sophisticated hierarchical micro-nanostructured anti-icing composites with photothermal, self-healable, and self-cleaning properties. However, few of them succeed in solving the problems of high-cost or ultra-complex fabrications.

More recently, candle soot nanoparticles have gotten enormous attention because of their inexpensive and photothermal performance. Extensive studies have proved that the candle soot-based surface can achieve superhydrophobic and photothermal icephobic performance [29–31]. The candle soot-based superhydrophobic photothermal surfaces can maintain a long-term ice-free state for the entire surface under the sun's illumination in a low-temperature environment. For example, the surface temperature of a candle soot-based superhydrophobic photothermal surface can increase by 53 °C under 1-sun illumination [31]. It relies on the excellent photothermal performance of candle soot on the micro/nanostructures of the surface. Obviously, the construction of the hierarchical micro/nanostructures is crucial to the robust anti/deicing ability of the candle soot-based photothermal superhydrophobic surface. However, most candle soot-based photothermal coatings tend to be unstable, and candle soot particles tend to fall off the coatings when impacted by water droplets or soaked in liquid. The unstable coating adds to the cost and complexity of the processing. In this regard, it is timely to develop an affordable and scalable strategy that enables the attainment of robust photothermal ice-repellent surfaces, which can efficiently delay ice formation and remove ice in an on-demand manner.

Here, we report a facile strategy to fabricate the candle soot-based photothermal surface (PDMS/CS60@PDMS/AI) that can gain heat through the absorption of sunlight. The key factor is the construction of the photothermal layer with hierarchical micro/nanostructures, which relies on the deposition of candle soot nanoparticles. By adding a certain amount of adhesive (PDMS), our candle soot-based photothermal coating shows mechanical durability even after a 200 cm sandpaper abrasion test. The PDMS/CS60@PDMS/AI surface still remains at a high water contact angle (~148°) under the action of an external force (1 N). Benefiting from the hierarchical micro/nanostructures, the PDMS/CS60@PDMS/AI surface exhibits excellent photothermal performance (high absorbance of ~96%). The photothermal layer in our work can be widely applied to various substrates except aluminum, such as Cu, stainless steel, and glass slides, endowing it with great potential in practical applications. Moreover, by combining with superhydrophobicity, the photothermal performance of the surface endows the PDMS/CS60@PDMS/AI surface further exhibits self-cleaning sunlight illumination, the PDMS/CS60@PDMS/AI surface further exhibits self-cleaning performance.

2. Materials and Methods

2.1. Materials

Polydimethylsiloxane (PDMS) prepolymer (Sylgard 184) and the curing agent were provided from Dow Corning, Midland, MI, USA; n-Hexane was obtained from Aladdin Biochemical Technology Co. Ltd., Shanghai, China; and the candle and polished aluminum (Al) sheets were purchased from the local market.

2.2. Fabrication of PDMS/Al Surface

The PDMS prepolymer and curing agent were first thoroughly mixed in a mass ratio of 10:1 and degassed in a vacuum chamber for 1 h. Then the PDMS solution was spin-coated onto the prepared Al substrate at 2000 rpm for 10 s. After the spin coating process, the sample was baked at 80 $^{\circ}$ C for 12 min to semi-harden the PDMS.

2.3. Fabrication of PDMS/Candle Soot@PDMS/Al (PDMS/CS@PDMS/Al) Surface

The PDMS/Al samples were first held above the flame of a candle to evenly deposit the candle soot (CS) layer. Subsequently, the mixed PDMS-n-hexene solution (PDMS: curing agent: n-hexene = 10:1:100) was sprayed onto the samples. After that, the samples were baked at 80 °C for 120 min to harden the PDMS. In this work, four sets of surfaces were fabricated by tuning the deposition time of CS for 10 s, 30 s, 60 s, and 120 s, respectively, which were denoted as PDMS/CS10@PDMS/Al, PDMS/CS30@PDMS/Al, PDMS/CS60@PDMS/Al, and PDMS/CS120@PDMS/Al, respectively.

2.4. Characterization of the PDMS/CS@PDMS/Al Surface

The surface morphologies of the PDMS/CS@PDMS/Al samples were observed by a field emission scanning electron microscope (FEI Scio 2 HiVac) with a low vacuum mode and an accelerating voltage of 5 kV. The amounts of C, O, and Si in the PDMS/CS@PDMS/Al samples were confirmed by using element dispersive spectroscopy. The variations of C 1s, O 1s, and Si 2p bonds of the PDMS/CS60@PDMS/Al surface were confirmed by using an X-ray photoelectron spectrometer (XPS) with an Al K α X-ray source (Thermo Scientific K-Alpha, Waltham, MA, USA, spot size ~400 μm²). The chemical compositions of the PDMS/CS60@PDMS/Al surface were examined by using a Fourier transform infrared spectrophotometer (FTIR, Nicolet 6700, Waltham, MA, USA). The absorbance in UV-Vis spectra of PDMS/CS@PDMS/Al samples was measured by using a spectrophotometer (UV-3600i Plus, Shimadzu, Long Beach, CA, USA). The relative thermal images of PDMS/CS@PDMS/Al samples were photographed by using an infrared thermal camera (A615, FLIR Systems, Wilsonville, OR, USA). Additionally, the static water contact angle and rolling angle of PDMS/CS@PDMS/Al samples were calculated with a Ramé-Hart goniometer (model 290-U1, Succasunna, NJ, USA). Droplets of \sim 5 μ L volume were gently deposited on the samples, and the contact angles were measured using the optical fiber goniometer. The mechanical stability is tested by using sandpaper abrasion. Firstly, 300-mesh sandpaper was used and fixed to the table. The PDMS/CS60@PDMS/Al surface was placed on the sandpaper. Then, a 100 g weight was pressed on the sample to provide the applied pressure. The PDMS/CS60@PDMS/Al surface was pulled on the sandpaper surface at different distances. The mechanical stability was characterized by the contact angle on the PDMS/CS60@PDMS/Al surface. The contact angle values were measured at every 20 cm distance. To ensure the repeatability of the results, all measurements were repeated at least three times.

2.5. Visualization of Droplet De-Icing and Anti-Icing Processes on the PDMS/CS60@PDMS/Al Surface

The droplet freezing experiment on the PDMS/CS60@PDMS/Al surfaces was carried out in a seal chamber. The relative humidity of the sealed chamber was maintained at 5% by filling in dry nitrogen and recorded by a humidity sensor (Testo 605i, Thermo-Hygrometer Smart Probe, Titisee-Neustadt, Germany). The low value of the relative humidity avoided the processes of condensation and frost formation. Initially, the samples were horizontally placed on the cooling stage (Cole-Parmer Standard Benchtop Chilling Block, Vernon Hills, IL, USA) with a preset temperature of -15 °C, -20 °C, and -25 °C, respectively. Then, a 10 µL droplet was deposited on the samples. The illumination of sunlight is carried out

by using a solar simulator. The droplet freezing process under 1-sun illumination was recorded by using two CCD cameras at 500 frames per second from the side view (EO-5032M, Navitar Zoom 6000, Burnsville, MN, USA) and the top view (WP-UT530M, Work Power, Shenzhen, CN). The de-icing process of the PDMS/CS60@PDMS/Al surface was carried out under one sunlight illustration and recorded by using the CCD camera from the top view (WP-UT530M, Work Power, Shenzhen, CN). The freezing statistics experiment was carried out in a sealed chamber with 5% relative humidity. The samples were horizontally placed on the cooling stage (Cole-Parmer Standard Benchtop Chilling Block) with a preset temperature of -15 °C. Then, with the illumination of 1-sun, the freezing dynamics of ~100 water droplets with a volume of 5 µL on the cooled bare Al surface (-15 °C) and on the cooled PDMS/CS60@PDMS/Al surface (-15 °C) were analyzed. The freezing delay time is defined as the time interval when the transparency of the frozen droplet changes from clear to opaque. The experiment was recorded by a CCD camera at 500 frames per second from the top view (WP-UT530M, Work Power). To ensure the repeatability of the results, all experiments were repeated at least three times.

3. Results

3.1. Fabrication and Characterization of PDMS/CS60@PDMS/Al

We constructed polydimethylsiloxane/candle soot60@polydimethylsiloxane/Aluminum (PDMS/CS60@PDMS/Al) based on the deposition of candle soot (CS) onto a PDMS/Al surface, where the photothermal performance of the CS layer can be tailored by controlling the deposition time. The PDMS/CS60@PDMS/Al was made through combined spincoating and vapor deposition technology. (Figure 1a). Briefly, to strengthen the CS layer and make the coating robust, a PDMS layer was first prepared by spin-coating the pure PDMS solution onto the Al surface (PDMS/Al) at 2000 rpm for 10 s. The PDMS/Al surface was then baked at 80 °C for 12 min to semi-harden the PDMS layer. After that, CS nanoparticles were facilely deposited evenly onto the PDMS/Al surface by holding it above the flame of a candle for 60 s. To induce low surface energy, a mixed PDMS/nhexene solution was sprayed onto the CS layer, and the sample was baked at 80 °C for 120 min. This three-layer surface, consisting of the underlying supporting PDMS layer, the middle photothermal CS layer, and the upper superhydrophobic PDMS layer, is termed the PDMS/CS60@PDMS/Al. For comparison, we also fabricated three sets of surfaces by governing the deposition time of CS nanoparticles within 10 s, 30 s, and 120 s, which were denoted as PDMS/CS10@PDMS/Al, PDMS/CS30@PDMS/Al, and PDMS/CS120@PDMS/Al, respectively. It should be noted that the photothermal CS layer in our work can be applied to some other substrates except aluminum. We can fabricate the photothermal CS layer on substrates such as Cu, stainless steel, and glass slides. There is only one condition the substrates should meet, namely, that they can be resistant to the high temperature of the flame of a candle (500 °C). Therefore, the photothermal layer in our work can be widely applied to various substrates, indicating great practical significance in many fields.

Figure 1b–e show the scanning electron microscopy (FEI Scios) images of PDMS/ CS10@PDMS/Al, PDMS/CS30@PDMS/Al, PDMS/CS60@PDMS/Al, and PDMS/ CS120@PDMS/Al, respectively. Owing to the incomplete combustion of candle flame [32–34]. CS nanoparticles are generated to form the CS layer on the as-fabricated surfaces. The interconnected CS nanoparticles have a diameter of 200 nm. With a 10 s deposition time, CS nanoparticles are seldom generated on the PDMS/CS10@PDMS/Al (Figure 1b). The amount of CS nanoparticles on the CS layer increases with the deposition time. After being deposited on the candle flame for 30 s and 60 s, the morphologies of CS layers show homogeneous micro-porous structures, which consist of increased CS nanoparticles (Figures 1c and 1d). These hierarchical micro/nanostructures of CS layers on the PDMS/CS30@PDMS/Al and the PDMS/CS60@PDMS/Al surfaces significantly enhance the surface roughness. However, when the deposition time is 120 s, too many CS nanoparticles agglomerate to form the CS layer [Figure 1e]. Due to the weak physical interactions between CS nanoparticles, the CS layer on the PDMS/CS120@PDMS/Al is too loose to form a strong bond with the underlying PDMS layer. Figure 1f,g show the cross-section micrographs of the PDMS/CS30@PDMS/Al surface and the PDMS/CS120@PDMS/Al, respectively. It can be seen that the thickness of the candle soot photothermal layer of the PDMS/CS30@PDMS/Al surface is smaller than that of the PDMS/CS120@PDMS/Al surface. Figure 1h shows the C mapping in the cross section of the PDMS/CS120@PDMS/Al surface. The PDMS/CS@PDMS/Al is further characterized by element dispersive spectroscopy (EDS) analysis according to the mapping in cross-section micrographs. It can be seen that the PDMS/CS30@PDMS/Al contains 63.5% of C, 22.5% of Si, and 14.0% of O (Figure 1i). The amount of C confirms the formation of the CS nanoparticles, while the amount of Si and O 1s indicates the existence of the PDMS layer. Furthermore, the content of C rises from 50.5% to 84.9% when the deposited time increases from 10 s to 120 s. The dramatic increase in C content is due to the fact that the main content of soot is branched saturated hydrocarbons. Furthermore, when the deposited time is 10 s, the content of the Si element is 31.8%. When the deposited time is 60 s, the content of Si decreases to 10.0%. The decrease in Si content is owing to the decomposition of PDMS during the deposition process.



Figure 1. Fabrication and characterization of PDMS/CS60@PDMS/Al. (a) Schematic drawing of the fabrication process of the PDMS/CS@PDMS/Al surface. FEI Scios images of (b) PDMS/CS10@PDMS/Al, (c) PDMS/CS30@PDMS/Al, (d) PDMS/CS60@PDMS/Al, and (e) PDMS/CS120@PDMS/Al, respectively. Cross-section micrographs for (f) PDMS/CS30@PDMS/Al and (g) PDMS/CS120@PDMS/Al surfaces. (h) EDS analysis of the PDMS/CS60@PDMS/Al. (i) The amount of C and Si for the surfaces with different deposited times.

Figure 2a shows the high-resolution XPS spectra of the Si 2p peak for the PDMS/CS60@PDMS/Al surface. The Si 2p peak can be deconvoluted into an organic Si peak at 102.3 eV and a SiO₂ peak at 103.4 eV [35]. This result proves that PDMS is decomposed during the candle soot deposition process, and part of organic Si is transformed into SiO₂. Furthermore, Figure 2a exhibits the FTIR spectrum of the PDMS/CS60@PDMS/Al surface. There are four peaks in the infrared spectrum that indicate the presence of a CH₃ group, namely, 2953 cm⁻¹ (stretching vibration), 1249 cm⁻¹ (in-plate bending vibration), 997 cm⁻¹ (out-of-plate bending vibration), and 774 cm⁻¹ (out-of-plate bending vibration). In combination with the XPS spectrum, it can be deduced that there is a physical interaction between the PDMS layer and the candle soot layer. The PDMS layer and the candle soot layer were successfully fixed on the PDMS/CS60@PDMS/Al surface. The static water contact angle and the rolling angle of the as-fabricated surfaces are shown in Figure 2c. The PDMS/CS10@PDMS/Al shows a static water contact angle of ~123° and a rolling angle

of ~14°, due to the lack of enough CS nanoparticles to form the micro/nanostructure of the CS layer on the surface. When the deposition time is greater than 30 s, the hierarchical micro/nanostructure of the CS layers endows the surfaces with superhydrophobicity. The surface roughness of the as-fabricated PDMS/CS@PDMS/Al is ~6 μ m [36–38]. Notably, the PDMS/CS60@PDMS/Al exhibits the largest water contact angle (~163°) and the smallest rolling angle (~1°). The mechanical stability of a superhydrophobic surface is important for practical application [39]. Figure 2d shows the PDMS/CS60@PDMS/Al surface was pulled on the sandpaper surface under 1 N. At the initial moment, the contact angle of the PDMS/CS60@PDMS/Al surface is ~163°. When the PDMS/CS60@PDMS/Al surface was pulled on the sandpaper surface for 100 cm, the contact angle was ~152°. Obviously, even after the 200 cm sandpaper abrasion test, the PDMS/CS60@PDMS/Al surface still remains at a high water contact angle (~148°). Therefore, the PDMS/CS60@PDMS/Al surface surface possesses mechanical durability under the action of external force.



Figure 2. Characterization of PDMS/CS60@PDMS/AI. (a) High-resolution XPS spectra of the Si 2p peak for the PDMS/CS60@PDMS/AI surface. (b) FTIR spectrum of the PDMS/CS60@PDMS/AI surface. (c) The static contact angle and rolling angle of the PDMS/CS10@PDMS/AI, PDMS/CS30@PDMS/AI, PDMS/CS60@PDMS/AI, and PDMS/CS10@PDMS/AI surfaces. (d) Mechanical stability test of the PDMS/CS60@PDMS/AI surface.

3.2. Photothermal Performance of PDMS/CS60@PDMS/Al

To examine whether the PDMS/CS60@PDMS/Al can achieve a sufficiently large heat to delay the freezing of water droplets by raising the surface temperature, we first investigate the photothermal performance of the PDMS/CS60@PDMS/Al under sunlight illumination. Figure 3a shows the absorbance of the PDMS/CS10@PDMS/Al, PDMS/CS30@PDMS/Al, PDMS/CS60@PDMS/Al, and PDMS/CS120@PDMS/Al, respectively. Beneficial to the nanoscale CS particles, the hierarchical micro/nanostructure of the CS layer can effectively trap and absorb light [40]. The absorbance of all the samples is approaching 96% throughout the visible and near-infrared light ranges. This remarkable absorption further improves the photothermal performance of the surfaces.



Figure 3. Photothermal performance of PDMS/CS60@PDMS/Al. (a) The absorbance of the asfabricated PDMS/CS@PDMS/Al surfaces throughout the visible and near-infrared light ranges. (b) Infrared images of the as-fabricated PDMS/CS@PDMS/Al surfaces at 15 min under 1-sun illumination. (c) Time-dependent temperature profile and (d) temperature-changing rate (dT/dt) of the irradiated area on the as-prepared PDMS/CS@PDMS/Al surfaces with 1-sun illumination.

The photothermal performance is then investigated based on the variation of surface temperature under 1-sun illumination (1 kW/m²). As is depicted in the infrared images in Figure 3b, the surface temperature sharply increases with the sunlight illumination time, which is sensitive to the deposition time of CS nanoparticles. The longer the deposition time is, the more obvious the temperature rise of the surface temperature of PDMS/CS10@PDMS/Al increases from 24.0 °C to 55.8 °C, whereas the surface temperature of PDMS/CS60@PDMS/Al increases from 24.0 °C to 63.1 °C (Figure 3c). Meanwhile, the maximum temperature rising rate (dT/dt) on the PDMS/CS60@PDMS/Al surface can reach ~10.3 °C/s (Figure 3d). This remarkable dT/dt on the PDMS/CS60@PDMS/Al is significantly higher than that on the other as-prepared surfaces, indicating superior photothermal performance (PDMS/CS60@PDMS/Al is used in the following section).

3.3. Anti-Icing Performance of PDMS/CS60@PDMS/Al

Due to the excellent photothermal property of the PDMS/CS60@PDMS/Al, anti-icing can be achieved on the surface under sunlight illumination. To evaluate the anti-icing performance of the PDMS/CS60@PDMS/Al, we investigated the freezing dynamics of the water droplet (10 μ L) on the cooled surface with sunlight illumination. As shown in Figure 4a, when a water droplet is deposited on the cooled bare Al surface (-15 °C) under 1-sun illumination, the droplet exhibits a hemispherical shape at 0 s (Video S1, Supplementary Materials). After 6 s, the droplet transforms from a transparent state to a non-transparent state and starts to freeze. The freezing front propagates from the bottom to the top until the droplet is completely frozen with a peach-tip shape at 26 s [41,42].



Figure 4. Anti-icing performance of PDMS/CS60@PDMS/Al with different surface temperatures. (a) Freezing process of a water droplet (10 μ L) on the cooled bare Al surface (-15 °C) under 1-sun illumination. (b) Freezing process of a water droplet (10 μ L) on the cooled PDMS/CS60@PDMS/Al surface (-15 °C) under 1-sun illumination (multi tiny droplets is circled by red dashed circles). (c) Freezing process of a water droplet (10 μ L) on the cooled PDMS/CS60@PDMS/Al surface (-20 °C) under 1-sun illumination. (d) Freezing process of a water droplet (10 μ L) on the cooled PDMS/CS60@PDMS/Al surface (-20 °C) under 1-sun illumination. (d) Freezing process of a water droplet (10 μ L) on the cooled PDMS/CS60@PDMS/Al surface (-25 °C) under 1-sun illumination. (e) Relation between portion of unfrozen droplets and freezing delay time on the cooled bare Al surface (-15 °C) and on the cooled PDMS/CS60@PDMS/Al surface (-15 °C) under 1-sun illumination. (f) Freezing delay time of the Al and the as-fabricated PDMS/CS@PDMS/Al surfaces. Heat transfer model between the droplet and the cooled (g) bare Al surface and (h) PDMS/CS@PDMS/Al surface with sunlight illumination. Scale bar: 1 mm.

However, on the cooled PDMS/CS60@PDMS/Al surface $(-15 \degree C)$, the droplet is spherical at the initial state (Figure 4b). Under 1-sun illumination, the droplet stays in a transpar-

ent state and does not freeze even after 7200 s. It confirms that the freezing of the droplet can be greatly delayed on the PDMS/CS60@PDMS/Al with the sunlight illumination. This freezing delay phenomenon is ascribed to two factors: one is the small contact area, and the other is the superior photothermal performance of the PDMS/CS60@PDMS/Al. The small contact area, which relies on the hierarchical micro/nanostructures of the CS layer, leads to a decrease in the heat conduction path between the droplet and the PDMS/CS60@PDMS/Al surface. Moreover, under 1-sun illumination, the favorable photothermal property of the surface enables the CS layer to continuously obtain more heat, which thus prolongs the freezing time. Notably, the volume of the droplet is reducing with time under 1-sun illumination. This is because droplet evaporation happens. After being illuminated by 1-sun, the PDMS/CS60@PDMS/Al surface gains huge heat transformed from sunlight due to its superior photothermal property. And the surface temperature of PDMS/CS60@PDMS/Al is rising. Therefore, the droplet deposited on the cooled PDMS/CS60@PDMS/Al surface $(-15 \,^{\circ}\text{C})$ experiences a temperature rise. After 7200 s, the volume of the droplet is smaller than the volume of the droplet at the initial moment (0 s). Furthermore, the droplet evaporation is accompanied by multiple tiny droplets forming on the solid-liquid-vapor three-phase contact line. The formation of multiple tiny droplets is due to the fact that there is a supersaturation pressure of water vapor on the solid-liquid-vapor three-phase contact line [43,44]. Under sunlight illumination, these multiple tiny droplets don't evaporate due to their small contact area on the surface and develop a ring pattern surrounding the deposited droplet (circled by red dashed circles). Further cooling the PDMS/CS60@PDMS/Al surface to -20 °C (Figure 4c), there also exists a tiny droplet ring pattern under 1-sun illumination (Video S2, Supplementary Materials). The droplet completely freezes after 2973 s. When the surface temperature of the PDMS/CS60@PDMS/Al decreases to -25 °C (Figure 4d), the droplet appears to be opaque at 124 s and freezes at 216 s with 1-sun illumination.

The freezing dynamics are characterized by using the freezing delay time, which is defined as the time interval when the transparency of the frozen droplet changes from clear to opaque. Figure 4e shows statistics of droplets freezing on the cooled Al surface $(-15 \,^{\circ}\text{C})$ and on the cooled PDMS/CS60@PDMS/Al surface $(-15 \,^{\circ}\text{C})$ under 1-sun illumination. As is depicted, all of the water droplets on the cooled Al surface freeze within 5 min, whereas the majority of water droplets on the cooled PDMS/CS60@PDMS/Al surface show a remarkable freezing delay of 1 h. This is because of the superior photothermal performance of the PDMS/CS60@PDMS/Al surface. As for the single droplet on the surface (Figure 4f), the freezing delay time on the cooled Al and the PDMS/CS60@PDMS/Al (-15 °C) under 1-sun illumination is ~ 6 s and ~ 7200 s. The freezing delay time decreases with the reduction in surface temperature. Remarkably, with a lower surface temperature of -25 °C, freezing delay can still happen on the cooled PDMS/CS60@PDMS/Al under 1-sun illumination, indicating the anti-performance of the PDMS/CS60@PDMS/Al. Furthermore, we compared the anti-icing performance between our work and the previous reports (Table 1). It can be seen that the water droplet freezing delay time is larger than that in the literature, indicating a superior anti-icing performance of the PDMS/CS60@PDMS/Al in our work.

Table 1. Comparison of anti-icing performance between the PDMS/CS60@PDMS/Al surface in this work and as-fabricated surfaces in the literatures.

Surfaces	Freezing Delay Time (s)	Reference
PDMS/CS60@PDMS/Al in this work	7200	This work
Bio-inspired micro-structure surface	1938	[1]
Nanostructured surface	1740	[15]
MWCNT based photothermal surface	1800	[45]
Cuttlefish juice based photothermal surface	144	[46]

3.4. Mechanism of Anti-Icing Permance of PDMS/CS60@PDMS/Al

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We then explore the underlying mechanism of anti-icing performance by establishing the heat transfer model between the droplet and the cooled PDMS/CS@PDMS/Al surface with sunlight illumination. As is shown in Figure 4g, the droplet on the cooled surface is considered a comprehensive solid-liquid-vapor three-phase system. When the droplet is deposited on the cooled Al surface with sunlight illumination, it gains heat from the air through heat conduction and heat radiation; it also obtains heat from sunlight; and it loses heat to the cooled Al surface through heat conduction and heat irradiation. The net heat gain of the droplet on the bare Al surface in unit time under sunlight illumination can be expressed as:

$$\Delta Q = Q_g + Q_s - Q_l \tag{1}$$

where ΔQ is the net heat gain of the droplet in unit time on the bare Al surface, Q_g is the heat gain of the droplet in unit time from the air, Q_s is the heat gain of the droplet in unit time from sunlight, and Q_l is the heat loss of the droplet in unit time to the cooled Al surface, respectively. Obviously, the droplet on the bare Al surface undergoes a fastfreezing process within 26 s (Figure 4a), indicating a small ΔQ of the droplet even after being illuminated by sunlight. As for the PDMS/CS60@PDMS/Al surface under sunlight illumination (Figure 4f), the droplet also gains heat from the photothermal surface in the form of heat conduction and heat radiation. The net heat gain of the droplet in unit time on the PDMS/CS60@PDMS/Al surface under sunlight illumination can be expressed as:

$$\Delta Q = Q_g + Q_s + Q_{pt} - Q_l \tag{2}$$

where Q_{pt} is the heat gain of the droplet in unit time from the PDMS/CS60@PDMS/Al surface under sunlight illumination. Notably, the additional heat transfer from the photothermal surface to the droplet leads to a large Q_{pt} , so the ΔQ of the droplet on the cooled PDMS/CS60@PDMS/Al surface is far larger than that of the droplet on the cooled bare Al surface. Moreover, the decreased temperature of the droplet in unit time during the freezing process can be expressed as:

$$\Delta T = \frac{\rho_w C_p (T_w - T_S)}{\Delta Q} \tag{3}$$

where ΔT is the decreased temperature of the water droplet, ρ_w is the water density, C_p is the heat capacity of water at constant pressure, T_w is the initial temperature of the water droplet, and T_s is the temperature of the cooled surface, respectively. It can be deduced that a smaller ΔT can be induced by a larger value of ΔQ , which results in a longer freezing delay time eventually.

Compared with that on the cooled bare Al surface (Figure 4f), a larger freezing delay time was observed on the cooled PDMS/CS60@PDMS/Al surface under the same experimental conditions. It reflects that the PDMS/CS60@PDMS/Al has superior photothermal performance and anti-icing ability. The mechanism of prolonged freezing delay on the cooled PDMS/CS60@PDMS/Al surface is further discussed in detail. The main reason for the prolonged freezing delay on the PDMS/CS60@PDMS/Al surface is related to the high energetic barrier and time lag for heterogeneous nucleation in the sessile droplet. According to the theory of nucleation kinetics [47], heterogeneous nucleation plays a major role in icing delay. The relation between the portion of unfrozen sessile droplets on the substrate is proportional to the area available for heterogeneous nucleation. This area between the sessile droplet and the surface is defined by the contact angle and the portion of wetted area. In terms of the PDMS/CS60@PDMS/Al surface, because of the higher apparent contact angle, the portion of wetted area is much less than for the bare Al surface. Moreover, the PDMS/CS60@PDMS/Al surface has a high energy barrier for heterogeneous nucleation. Thus, the freezing delay for the PDMS/CS60@PDMS/Al surface is larger than that for the bare Al surface.

The anti-icing property is further demonstrated by analyzing the freezing behaviors of droplets (10 μ L) with various values of PH on the PDMS/CS60@PDMS/Al surface at -15 °C under 1-sun illumination. As is shown in Figure 5a–c, an HCl droplet (PH = 1), a NaCl droplet (PH = 7), and a NaOH droplet (PH = 14) are deposited on the cooled PDMS/CS60@PDMS/Al surface, respectively. With 1-sun illumination, all of the droplets are spherical at the initial state, indicating that the contact areas of the droplets with different PH values are all small enough to hinder the heat transfer from the droplets to the cooled PDMS/CS60@PDMS/Al surface. Due to the temporary increase of the surface temperature under sunlight illumination, flash evaporation happens on the HCl droplet, the NaCl droplet, and the NaOH droplet. Among them, the HCl droplet shows the fastest evaporation rate and is surrounded by a ring pattern (circled by red dashed circles). This fast evaporation of the HCl droplet is attributed to the existence of a large supersaturation gas pressure, which is triggered by the easily volatilized HCl molecular weight (Figure 5a). Meanwhile, some white NaCl crystals form when the NaCl droplet vaporizes (Figure 5b). The formation of the NaCl crystals may be due to the fact that there is a circular flow inside the NaCl droplet caused by the Marangoni effect [48,49]. Under sunlight illumination, the Marangoni flow carries the NaCl particles with it and accumulates them on the bottom of the NaCl droplet. When the surface is illuminated by sunlight after 7200 s, all of the droplets with different PH values are not frozen on the PDMS/CS60@PDMS/Al surface (Figure 5c).



Figure 5. Anti-icing performance of PDMS/CS60@PDMS/Al in terms of droplets with different PH values. Freezing process of (**a**) an HCl droplet (PH = 1, multi tiny droplets is circled by red dashed circles), (**b**) a NaCl droplet (PH = 7), and (**c**) a NaOH droplet (PH = 14) on the cooled PDMS/CS60@PDMS/Al surface (-15 °C) under 1-sun illumination, respectively. (**d**) Freezing process of a mud droplet (10 µL) on the cooled PDMS/CS60@PDMS/Al surface (-15 °C) under 1-sun illumination. Scale bar: 1 mm.

In addition, in terms of a mud droplet freezing on a cooled PDMS/CS60@PDMS/Al surface (-15 °C) under 1-sun illumination (Figure 5d), the freezing process can be accelerated by two factors [50]. The first is the inherent non-transparent state of the mud droplet, which strongly lessens the photothermal performance due to the fact that sunlight cannot pass through the mud droplet to the surface. The second is the existence of undesirable ice nucleation sites in the mud droplet, which are generated from the mud particles and can further speed up the mud droplet freezing process. Nevertheless, the mud droplet on

the cooled PDMS/CS60@PDMS/Al surface still shows a freezing delay phenomenon with 1-sun illumination. The mud droplet does not completely freeze before ~807 s. Furthermore, there is an annular flow on the top side of the mud droplet due to the Marangoni effect. Therefore, the mud droplet forms a flat pattern when it is completely frozen. The above-mentioned results prove that our PDMS/CS60@PDMS/Al can not only be applied to anti-icing with different surface-cooled temperatures but also to practical anti-icing for droplets with various values of PH as well as for droplets in the mud environment.

3.5. De-Icing Performance and Self-Cleaning Performance of PDMS/CS60@PDMS/Al

De-icing can also be realized on the PDMS/CS60@PDMS/Al under sunlight illumination. As depicted in Figure 6a,b, an ice layer with a thickness of 4 mm was allowed to accumulate on the cooled bare Al surface and the cooled PDMS/CS60@PDMS/Al surface $(-15 \,^{\circ}\text{C})$ in advance, respectively. After being illuminated by 1-sun for 1710 s, the ice layer on the cooled bare Al surface does not melt. By contrast, with the same illumination time of 1-sun, the ice layer on the cooled PDMS/CS60@PDMS/Al surface completely melts. Note that the rolling angle of the PDMS/CS60@PDMS/Al surface is $\sim 1^{\circ}$. Most of the melted water droplets can roll off the surface. The outstanding ice-repellency of the surface is attributed to the synergistic cooperation of the excellent photothermal performance and the superior superhydrophobicity. Furthermore, the PDMS/CS60@PDMS/Al also shows a self-cleaning feature. As shown in Figure 6c, the cooled PDMS/CS60@PDMS/Al surface $(-15 \,^{\circ}\text{C})$ was first covered by opaque contaminants (Al₂O₃ powders). The contaminants can be easily removed by continually injecting water flow to the surface. The injected water droplets do not freeze and can easily slide away with 1-sun illumination. It reflects that the PDMS/CS60@PDMS/Al possesses the self-cleaning ability to avoid the contaminants covering the surface and to guarantee outstanding photothermal performance.



Figure 6. De-icing and self-cleaning performance of PDMS/CS60@PDMS/Al. An ice layer (thickness ~4 mm) melting process on (**a**) the cooled bare Al and (**b**) the cooled PDMS/CS60@PDMS/Al surface (-15 °C), respectively. (**c**) Contaminants on the cooled PDMS/CS60@PDMS/Al surface (-15 °C) are removed by injecting water flow under 1-sun illumination. Scale bar: 10 mm.

4. Conclusions

In summary, we develop a novel candle soot-based superhydrophobic surface (PDMS/CS60@PDMS/Al) for photothermal anti-icing and de-icing. The hierarchical micro/ nanostructures of the as-fabricated PDMS/CS60@PDMS/Al endow the surface with high absorbance (~96%) throughout the visible and near-infrared light range. Under 1-sun sunlight illumination, the surface temperature rises from 24.0 °C to 63.1 °C within 15 min, and the maximum temperature rising rate (dT/dt) on the PDMS/CS60@PDMS/Al surface can reach ~10.3 °C/s, indicating a superior photothermal performance. Such a large temperature rising rate (dT/dt) of the PDMS/CS60@PDMS/Al makes it easier to delay freezing for droplets with various values of PH or droplets in the mud environment. The

freezing delay time can be prolonged to ~ 7200 s to hold back the ice formation at a subzero surface temperature of -15 °C with 1-sun illumination. The underlying mechanism is elucidated by establishing the heat transfer model between the droplets and the cooled surface. Furthermore, benefiting from the superhydrophobicity and excellent photothermal performance, after being illuminated by sunlight, the PDMS/CS60@PDMS/Al surface can achieve rapid melting of the interface ice layers, inducing the multi-abilities of de-icing and self-cleaning. We envision that this work could open a new avenue for the development of novel photothermal surfaces to enhance anti-icing, anti-frosting, and de-icing abilities for practical applications in subzero temperature environments.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/coatings14050612/s1, Video S1: Freezing process of a water droplet on the cooled Al surface (-15 °C) under 1-sun illumination; Video S2: Freezing process of a water droplet on the cooled PDMS/CS60@PDMS/Al surface (-20 °C) with 1-sun illumination.

Author Contributions: Conceptualization, X.C.; methodology, X.C., C.Q. and L.W.; validation, C.Q. and L.W.; formal analysis, C.Q., L.W. and X.C.; writing—original draft preparation, C.Q., L.W. and X.C.; writing—review and editing, X.C. and Q.L.; supervision, X.C. and Q.L; project administration, X.C. and Q.L.; All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the National Natural Science Foundation of China (52276071 and U2241252).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Data are contained within the article.

Conflicts of Interest: The authors declare no conflicts of interest.

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Review Soft Feel Material Coatings on the Surface of Plastic Products and Their Application Prospects in the Popular Fields: A Review

Bangzheng Jiang ^{1,2}, Yueyang Xu ^{1,2}, Lanlan Zhang ^{3,*}, Xing Zhou ^{2,4}, Hui Zhang ¹, Luqi Liu ¹ and Jun Zhao ^{1,5,*}

- ¹ CAS Key Laboratory of Nanosystem and Hierarchical Fabrication, CAS Center for Excellence in Nanoscience, National Center for Nanoscience and Technology, Beijing 100190, China; jiangbz2024@nanoctr.cn (B.J.); xuyy2023@nanoctr.cn (Y.X.); zhangh@nanoctr.cn (H.Z.); liulq@nanoctr.cn (L.L.)
- ² Faculty of Printing, Packaging Engineering and Digital Media Technology, Xi'an University of Technology, Xi'an 710048, China; zdxnl@xaut.edu.cn
- ³ Shenzhen ShineCMF Advanced Materials Co., Ltd., Shenzhen 518107, China
- ⁴ School of Materials Science and Engineering, Xi'an University of Technology, Xi'an 710048, China
- ⁵ College of Materials Science and Optoelectronic Technology, University of Chinese Academy of Sciences, Beijing 101408, China
- * Correspondence: lan@shinecmf.com (L.Z.); zhaoj@nanoctr.cn (J.Z.)

Abstract: Soft-feel material (mainly polyurethane (PU), silicone rubber (SR), and polyacrylic acid (PAA), etc.) coatings can overcome the drawbacks of common plastic products such as acrylonitrile butadiene styrene copolymer (ABS), polycarbonate (PC), and polypropylene (PP), which have cold, hard, and bright surfaces, achieving warm, soft, and matte effects, thus greatly improving the quality and price level of the products. Although these coating materials can partially meet the main requirements of the soft feel effect, their comprehensive properties, such as mechanical performance, weather resistance, and foul resistance, still have shortcomings and need to be improved. Besides, there is a lack of in-depth exploration in the literature on the design philosophy and preparation strategies of soft-feel materials. Starting from the mechanism of producing this comfortable feeling and then systematically exploring their application in popular fields with high economic added value, such as mobile phone cases, electronic cigarette cases, cosmetic containers, etc., this article attempts to systematically and meticulously review the research and development progress in the related fields in recent decades and tries to provide an open outlook on their future development directions, e.g., the employment of surface engineering and hybrid materials. This review is expected to provide some rational thinking directions and convenient practical guidance for the rapid and healthy development of soft-feel materials in the research and application fields.

Keywords: soft feel material; polyurethane (PU); acrylonitrile butadiene styrene copolymer (ABS); coating; mobile phone case

1. Introduction

Compared with traditional metal and ceramic materials, plastic, one of the polymer materials, has many advantages, such as light weight, corrosion resistance, easy processing, low preparation energy consumption, and easy realization of complex shapes in parts. Therefore, it is gradually replacing traditional materials in many fields. Among them, the plastic materials are particularly in line with the development requirements of light weight, low energy consumption, and low emissions in the automotive industry and are therefore widely used in automotive components [1]. For example, Thomas et al. provided a systematic review of the latest developments in two important automotive external plastic substrates, thermoplastic polyolefin (TPO) and polycarbonate (PC), with a focus on their coating materials [2].

Citation: Jiang, B.; Xu, Y.; Zhang, L.; Zhou, X.; Zhang, H.; Liu, L.; Zhao, J. Soft Feel Material Coatings on the Surface of Plastic Products and Their Application Prospects in the Popular Fields: A Review. *Coatings* **2024**, *14*, 748. https://doi.org/10.3390/ coatings14060748

Academic Editors: Jose Maria De Teresa, Ricardo Lopez Anton and Sion Federico Olive Méndez

Received: 15 May 2024 Revised: 10 June 2024 Accepted: 11 June 2024 Published: 13 June 2024



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As an outstanding representative of plastic materials, acrylonitrile butadiene styrene (ABS) copolymer resin is an engineering plastic, and its excellent comprehensive performance comes from the synergistic effect among the acrylonitrile with high chemical corrosion resistance and surface hardness, the butadiene with high toughness, and the styrene with good processing and dyeing properties [3]. Therefore, ABS resin has been widely used in interior and exterior decorations such as door panels, instrument panels, and heat dissipation grilles in automobiles, as well as in electronic products such as mobile phone cases and computer components. However, its products are prone to defects such as uneven colors and blemishes, and there are also issues such as aging, brittleness, scratches, contamination, and static electricity accumulation during use. It has been known that the surface coatings, especially the soft-feel materials, can cover the defects and give a certain color and luster, thereby improving the beauty and comfort of their appearance. In addition, it can also provide a certain protective effect on the substrate, preventing it from being corroded by scratches, solvents, rain, snow, etc. For example, polyurethane (PU) soft-feel coatings can significantly improve the scratch resistance, wear resistance, solvent resistance, and other properties of the ABS resin surface. They can also reduce the gloss to 1% in the 60° direction and reduce the friction noise [4].

The demand for soft-feel coatings from consumers for hard plastic products such as ABS, PC, and polypropylene (PP) with a leather-like soft and smooth touch and a matte appearance has led to the emergence of soft-feel coatings. Bayer, a German company, was the first to develop the first generation of soft-feel coatings in the 1990s. Afterwards, in terms of raw material synthesis and preparation technology for the soft-feel coatings, it has also been at the forefront of the world [4]. Soft-feel coating is also known as elastic coating, elastic paint, elastic touch coating, rubber coating, rubber paint, touch coating, touch paint, etc. Its name is precisely because it can change the drawbacks of plastic products being cold, hard, and shiny, giving people a warm, flexible, delicate, and smooth texture. At present, the plastic substrates widely used for soft-feel coatings in consumer goods mainly include automotive interiors (such as instrument dials, handles, etc.) and electronic products (such as computer components, mobile phone cases, electronic cigarettes, etc.) that come into direct contact with the human body. In the past decades, soft-feel coatings have shifted from an early pursuit of elasticity similar to skin or soft rubber to achieving a velvet-like, silky, dry, and soft overall texture. In terms of its materials, it mainly includes PU, silicone rubber (SR), and polyacrylic acid (PAA), among which PU occupies a dominant market share. Generally speaking, compared with SR, PU has better transparency, softness, and stain resistance but is more prone to yellowing and less prone to demolding.

Zhao pointed out that to prepare the soft felt PU coating on the surface of biaxially oriented polypropylene (BOPP) films, there were three different strategies: using the soft and highly elastic PU microspheres, using the waterborne polyurethane (WBPU) selfmatting lotion, and using the excimer ultraviolet light (UV) curing to induce the wrinkling of the surface [5]. It is worth noting that so-called soft materials usually refer to synthetic materials and biomaterials with an elastic modulus below 10 MPa. They have excellent characteristics such as light weight, low modulus, and stretchability, as well as various functions such as sensing, actuation, insulation, and transportation. Therefore, they can be applied in many fields, such as smart textiles, flexible devices, wearable electronic products, and so on. Li et al. systematically reviewed the progress in the design, preparation, and application of soft materials from the three categories of gel, foam, and elastomer [6].

Although there have been some reviews in the literature on the definition, composition, characteristics, and detection methods of soft-feel coatings, the analysis of this field still lacks depth and breadth [4]. As shown in Figure 1, this review starts with the functions and application requirements of soft-feel materials. Then, through the in-depth and detailed exploration of the formation mechanism and influencing factors of soft feel, the research and development history and current status of soft feel materials, and the common characteristics of soft feel materials, new solutions will be proposed for the application of soft feel materials in high-value products such as mobile phone cases.



Figure 1. Schematic presentation of the main content of this review.

2. Formation Mechanisms and Influencing Factors of Soft Feel

The hedonic properties of tactile stimuli, including soft feel, are crucial for the quality of human life [7]. It is generally believed that soft and smooth material surfaces are pleasant, while hard and rough material surfaces are unpleasant. Essick et al. found that the tactile sensation not only depended on the characteristics of the material surface but was also influenced by many factors, such as the perceptual parts of the human body, contact speed, pressure level, human gender, and the roughness of finger skin [8]. In addition, the difference between the hot and cold sensations of fingers caused by the high or low ambient temperature also played an important role in tactile pleasure. Cavdan et al. believed that the soft feel of an object was the result of the joint perception of different senses, such as touch and vision [9]. Among them, the tactile perception focused on the flexibility, viscosity, particle size, and roughness of the materials, while the visual perception could also provide similar information, especially since there was a strong correspondence between dynamic vision and tactile perception.

Interestingly, Bai et al. pointed out that the generation of skin sensation on the surface of objects was due to the existence of special structures such as wrinkles and bumps, which caused people to develop self-awareness during contact with them [10]. Based on the formation mechanism of skin sensation boards, they also reviewed the forming methods of skin sensation board coatings, skin sensation evaluation indicators, etc., in order to contribute to the production of skin sensation furniture.

Liu et al. conducted subjective tactile tests on 10 materials, including natural wood, leather, engineering plastics, and metal, used to prepare automotive internal components [11]. These tests included smoothness/roughness, softness/hardness, flexibility/resistance, as well as warmth/coldness, and they were compared with the functions obtained from the tribological probe microscopy (TPM) tests such as morphology, friction, Young's modulus, hardness, etc. The results indicated that although there was a significant difference in the perceived area scale between the two, there was still a strong correlation between them, indicating that human tactile perception was indeed influenced by the microstructure and even nanostructure of the material surface.

Similarly, Mirabedini et al. prepared the soft feel coatings using water-based resins composed of soft and hard PU resins, studied the effects of raw material composition and content on the soft feel performance, and attempted to find the correlation between the user perception and the experimental measurement characteristics of the coating surface [12]. For this purpose, they organized 72 people to touch the coating in a similar testing en-

vironment and give ratings while characterizing the physical properties of the coating through measurements such as mechanical stretching, micro-Vickers hardness, atomic force microscopy (AFM), and friction coefficient. The results showed that the soft feel effect of the material was the best when the ratio of soft and hard resin was 1:3. Interestingly, the films with the best tactile effect were not the ones with the lowest or highest hardness, but the coatings with the highest flexibility. In addition, the best coating for soft feel had a lower coefficient of friction and lower surface roughness, but the coating with the lowest coefficient of friction was not good for soft feel. As shown in Figure 2, surface roughness is inversely proportional to the soft feel effect, which means that a rough surface can reduce the soft feel effect. Overall, there was good consistency between the comprehensive properties such as mechanical properties, surface roughness, and friction coefficient and the human touch, making it a standard for predicting and evaluating the soft feel effect of materials. The coatings with the best soft feel effect were those with higher hardness, medium modulus, lower roughness, and a lower friction coefficient.



Figure 2. Correlation between the coating surface roughness and the soft feel effect (modified from Reference [12] with permission).

Generally speaking, the friction coefficient of soft objects with lower elastic modulus and hardness is greater than that of hard objects with higher elastic modulus and hardness. Arakawa et al. used some powders to coat the skin, like materials made of PU, and then conducted the psychophysical experiments [13]. However, they found that for surfaces with the same elastic modulus, the lower the friction coefficient, the better the soft feel. In contrast, when only pressing, there was no such difference. They believed that, from the perspectives of tribology and contact mechanics, the psychophysical interference between hardness (elastic modulus) and friction coefficient was a paradox, and the incorrect separation between normal and tangential forces and skin deformation at the finger pad might be the main reasons for this paradox in humans.

Considering that soft feel, as a manifestation of the value of an item, is usually determined by the subjective sensory evaluation of consumers and has the drawbacks of being time-consuming and costly, Hashim et al. were inspired by human perceptual flow and proposed a tactile evaluation system based on tactile layering, which provided tactile feedback from the output of sensors [14]. They classified the tactile sensation from low tactile sensation (LTS) to high tactile sensation (HTS) and then obtained the correlation between each level through the statistical analysis. Based on the physical measurements, preferences were determined, and tests showed an accuracy rate of up to 80%. As can be seen from the above, the soft feel is indeed related to the material and hierarchical structure of the item, which also provides guidance for the design and preparation of soft feel materials. For example, by cleverly combining the surface materials with hierarchical structures, an unprecedented soft feel can be created. The testing of soft-feel performance still requires a more objective and repeatable approach. Only in this way can soft feel be transformed from subjective qualitative property to objective quantitative performance, and a series of standards can even be generated for the related industry to follow.

3. Design, Preparation, and Characterization of PU Soft Feel Materials

3.1. The Basic Composition of PU Soft Feel Materials

The soft-feeling materials not only need to have the comfort of skin touch and the elegance of vision but also need to have advantages such as good resistance (scratch resistance, corrosion resistance, and solvent resistance), low glossiness, and low production of volatile organic compounds (VOCs). The VOC production of water-based coatings can be less than 4 g/m², while that of solvent-based coatings is generally higher than 80 g/m² [15]. Obviously, compared with the oil-based coatings using organic solvents, the water-based coatings using water as a solvent are more in line with environmental protection requirements and therefore have a much higher proportion in automotive interior coatings than in exterior coatings [16]. Actually, by introducing metal coating on the polymer substrate, we can also reduce the release of VOCs and realize some interesting functions [17,18], but that is not the focus of this review.

As mentioned earlier, the materials used for soft feel mainly include PU, SR, and PAA, but PU holds a much larger market share than others. Therefore, PU will be the focus of this review. Of course, there are also some reports in the literature on other types of soft-feel materials. For example, Na et al. considered that leather, fur, feathers, and other materials used as friction-positive electrode materials had good tactile properties (comfort) [19]. Therefore, they melted and mixed eggshell membrane (ESM) powders, which were also friction-positive electrode materials, with PP and found that the prepared ESM/PP biocomposite materials had enhanced tactile properties. The main mechanism was that the addition of polar ESM reduced the in-plane friction coefficient of non-polar PP and increased its frictional positivity, surface smoothness, and adhesion. In addition, Wang et al. selected the hydroxyl-modified PAA resin as the film-forming material to prepare a two-component soft-feel coating for ABS plastics, which had a smooth hand feel, good scratch resistance, and excellent adhesion [20]. The effects of the types and contents of the main components (plasticizers, matting agents, curing agents, solvents, additives, etc.) on the main properties of the paint film (adhesion, soft feel degree, scratch resistance, etc.) were discussed. They first prepared component A (including hydroxymodified PAA resin, thermoplastic PAA resin, pigment, filler, matting agent, dispersant, drying agent, leveling agent, solvent, etc.), and then mixed it evenly with component B (mainly including a mixture of curing agent, diluent, etc.) in a certain proportion and adjusted the viscosity before spraying it onto ABS sheets cleaned with anhydrous ethanol. After repeating 2–3 times, the coating was dried at room temperature for 10–15 min and then baked at 80 $^{\circ}$ C for 30–40 min. The final coating thickness was about 30 μ m. The results showed that the optimized raw material formula included the curing agent N-3390, the matting agent organic agent OK607, the drying agent dibutyltin dilaurate (DBTDL), the leveling agent organic silicon agent BYK331 and the fluorocarbon modified acrylic agent EFKA3777.

PU was invented by Otto Bayer from Germany in 1937 [21] and began to be used as a coating for airplanes around 1960. PU is divided into polyester type and polyether type, which can be used to prepare materials with different apparent properties, such as plastics (mainly foam plastics), fibers (spandex), and elastomers [22–26]. Its chemical reaction is the condensation polymerization of polyisocyanate (such as hexamethylene diisocyanate (HDI)

trimer, biuret, etc.) curing agents with diols (polyester, polyether, or other types) [27–29], with the general reaction formula being:

$$-N=C=O + -OH \rightarrow -NH-COO-$$
 (1)

It should be noted that isocyanates can easily react with water to produce urea:

$$2-N=C=O+H_2O \rightarrow -NH-CO-NH-+CO_2$$
(2)

Therefore, in a water environment, the amount of isocyanate groups (-N=C=O) added (whose content changes can be measured by Fourier transform infrared spectroscopy (FTIR)) needs to be slightly higher than that of the hydroxyl group (-OH) of polyols. In addition, polyisocyanates are generally hydrophobic, so emulsifiers or polyhydroxy resins need to be added for emulsification.

The composition of PU soft feel coatings generally includes an elastic resin matrix, curing agent, drying agent (catalyst), elastic powder, soft feel additive, matting powder, leveling agent, wetting agent, organic solvent, additive, etc. The main materials that provide soft feel performance are elastic resin matrix, elastic powder, and soft feel additives. The water-based PU soft feel coating is usually composed of highly elastic WBPU dispersions and waterborne polyisocyanates. The high elasticity of PU coatings comes from linear, long chains combined with moderate crosslinking. Leveling agents and wetting agents are mainly used to improve the uniformity of coatings, while wax additives (such as Brazilian palm wax) can produce a smooth surface casmir.

The rigid part of PU determines its hardness and high-temperature properties, while the flexible part determines its elasticity, low-temperature properties, hydrolysis resistance, and solvent resistance. The main difference between PU soft-feel coatings and regular topcoats is that the former has more flexible parts and a lower crosslinking density. Therefore, they have better low-temperature resistance but may have poorer solvent resistance. It seems that there is indeed a certain contradiction between the soft-feel characteristics of PU soft-feel coatings and their solvent resistance, so it is necessary to make certain compromises in practice according to specific application requirements.

3.2. Specific Formula, Performance Testing, Preparation Methods, and Research and Development Progress of PU Soft Feel Materials

3.2.1. The Specific Formula of PU Soft Feel Materials

Table 1 lists several typical formulas for PU soft-feel materials, among which some are also their optimized formulas. It can be seen that its main formulas include elastic resin, curing agent, drying agent, elastic additive, matting powder, leveling agent, diluent, and additive, etc. Among them, there are the most diverse types of additives, each playing a different role.

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Coatings

	Additive	ı	420 anti-settling agent, 346 wetting agent, and 024 defoamer (BYK, Germany)	ı	190 and 191 wetting agent, 024 defoamer, and 420 thickener (BYK, Germany)	(BYK, Germany)
	Diluent	7400	190 (BYK, Germany), DMPA, N- methylpyrrolidone, TEA, and triethylenediamine	Xylene, toluene, butyl acetate, ethyl acetate, diacetone alcohol, and solvent oil S1000	·	Commercially available
	Leveling Agent	ALF10 and AL106	381 (BYK, Bertelsdorf, Germany)	331 and 358 (BYK, Germany)	348 (BYK, Germany)	Organic silicon and fluorocarbon modified PAA
	Matting Powder	AL519	·	OK500, OK520, and TS100 (Degussa, Dusseldorf, Germany)	N20 (Wacker, Germany)	Commercially available
· ·	Elastic Additive	AS340 and CS554 powder	ı	1	P800T podwer (Genshin, Tokyo, Japan) and wax dispersion CERAF-LOUR929	
	Drying Agent	AKL25 and AS337	DBTDL	DBTDL	ı	Commercially available
	Curing Agent	09WN	IPDI and HDI	L75, N3390, and N75 (Bayer, Leverkusen, Germany)	Aliphatic isocyanates	L75, N3390, and N75 (Bayer, Germany)
	Elastic Resin	PL1300 and PS301	Polyester polyols	CTR6426 and CTR6428 polyester (CNOOC Changzhou Environmental Protection Coatings, China)	PC polyols	PAAA and hydroxyl modified PAA (CNOOC Changzhou Environmental Protection Coatings, Changzhou, China)
	References	[30]	[31]	[32]	[15]	[20]

Table 1. The (optimized) formula of PU soft-feel materials (sorted by the publication date of literature).

3.2.2. Performance Testing of PU Soft Feel Materials

The performance testing of PU soft feel materials mainly includes drying time, film thickness, adhesion, pencil hardness, glossiness (60°), flexibility, soft feel (including softness, smoothness, and elasticity), scratch resistance, impact resistance, wear resistance, water resistance, solvent resistance (such as ethanol, butanone, etc.), acid alkali salt resistance, high temperature and high humidity resistance, etc. (as shown in Table 2). Among them, there are two kinds of characterization methods for soft feel: the hand-touch method and the physical detection method. The hand-touch method is to directly touch it with your hand and then rate it based on your value perception. Although this method is convenient, fast, and widely used, it lacks quantitative indicators and is greatly influenced by human factors. The physical detection method subdivides the tactile sensation into four aspects: rough/smooth, soft/hard, cold/hot, and dry/wet, and strives to set quantitative indicators. It is an improvement on the hand touch technique, but there is still a significant gap from true quantification.

Table 2. Performance testing of PU soft-feel materials and the Chinese national testing standards adopted.

Performance	Testing Methods	References
Adhesion	Hundred grid knife scratching methods, levels 1–7, with level 1 being the strongest	[33]
Pencil hardness	9B–9H, with 9H being the hardest	[34]
Glossiness (60°)	-	[35]
Flexibility	Level 1–7, with level 7 being the highest	[36]
Soft feel	Hand touch technique, level 1–5, with levels 5 being the best	-
Scratch resistance	Fingernail method, level 1–5, with levels 5 being the strongest	-
Impact resistance	-	-
Wear resistance	-	-
Water resistance	-	-
Solvent resistance (such as ethanol, butanone, etc.)	Number of solvent wiping cycles	[37]
Acid, alkali, and salt resistance	-	-
High temperature and high humidity resistance	-	-

3.2.3. Preparation Methods and Research Progress of PU Soft Feel Materials

The earliest PU soft feel materials were achieved through the elasticity of polyester main chains, but their water resistance and yellowing resistance were poor, and harmful chemicals such as triethylamine (TEA) were included in the formula. From 2008 to 2009, Bayer Company launched an elastic tactile coating composed of a dispersion containing hydroxyl groups and polyisocyanates, which could react to form a rubber-like coating. In addition, high-molecular-weight nonreactive PU crosslinks were also added to the system to achieve a velvet-like, soft, and dry feel.

Chen used a certain proportion of PL1300 and PS301 resins as elastic resins and added curing agents, drying agents, tactile additives, elastic powder, matting powder, leveling agents, etc. to prepare soft-feel paint [30]. The optimized formula obtained was: the ratio of two polyester resins in the elastic resin was 1:1; the amount of drying agent was 2 wt% of the total resin amount; the amount of curing agent was 1.1 times the equivalent amount; the amount of tactile agent was 10 wt% of the total resin amount; the amount of matting powder was 5 wt% of the total resin amount. The 15–20 µm primer was first sprayed, and then the 25–30 µm topcoat was sprayed. The difference between the two was that the latter had more curing agents

and diluents added than the former. A 200-mesh filter cloth was used before spraying, and the coating was air dried for 15–20 min after spraying and then baked at 80 $^\circ$ C for 30 min.

Xu et al. introduced pentaerythritol triacrylate (PETA) and polydimethylsiloxane (PDMS) into the main chain of WBPU to prepare the siloxane-modified WBPU lotion that could be cured by UV, and then compounded the lotion with additives to prepare waterborne coatings [38]. Compared with the unmodified coatings, the modified coating had good water and solvent resistance while retaining excellent soft feel and could be used as a water-based soft feel coating. Among them, the silicone polymer segments gave the material a good soft feel, while the UV curing gave it the required crosslinking density. The raw materials included isophorone diisocyanate (IPDI), PDMS, polytetrahydrofuran ether glycol (PTMG), dihydroxymethylpropionic acid (DMPA), butanediol (BDO), PETA, TEA, DBTDL, photo initiators Irgacure 1173 and Irgacure 500, and additives. In the process of coating preparation, the WBPU lotion was prepared first, and then the photoinitiator, wetting agent, leveling agent, defoamer, thickening agent, and water were added.

Zhou et al. synthesized the WBPU dispersions with or without hydroxyl end groups using polyester polyols and diisocyanates, respectively. After mixing, defoamers, leveling agents, dispersants, wetting agents, anti-settling agents, and other additives were added, and then reacted with hydrophilic aliphatic polyisocyanate curing agents to prepare the two-component WBPU soft feel coatings [31]. The main raw materials included IPDI, HDI, polyester polyols, DMPA, N-methylpyrrolidone, TEA, DBTDL, triethylenediamine, leveling agent, defoamer, anti-settling agent, wetting agent, and dispersant. After the paint film was prepared and the surface was dried, it was baked at 80 °C for 30 min, and then left at room temperature for 2 d. They found that as the molecular weight of polyester polyols or the -OH/-N=C=O ratio increased, the flexibility, impact resistance, and scratch resistance of the paint film improved, but its adhesion, hardness, and solvent resistance decreased. The main reason was that the crosslinking density decreased. The preferred polyester polyol had a molecular weight of 2000 g/mol, the -OH/-N=C=O ratio was 1.6 for dispersion, and the -OH/-N=C=O ratio was 0.65 for curing.

Zhang et al. used polyester resin as the film-forming material, combined with matting powder, catalyst (DBTDL), solvent, leveling agent, curing agent, etc., to prepare an elastic tactile coating for ABS resin [32]. Firstly, polyester resin, solvent, catalyst, matting powder, and leveling agent were mixed, and then curing agent and diluent were added until the viscosity reached 15–18 s. ABS panels were cleaned with isopropanol to remove dust and oil stains. After spraying, the surface was dried for 10 min, and then baked at 60 °C for 30 min or dried at room temperature for 24 h. They found that the silicone leveling agents could provide smoothness, while the acrylic leveling agents could provide a leather-like feel. The optimized formula was linear hydroxyl polyester, TS100 matting powder, organic silicon leveling agent, DBTDL catalyst, and -N=C=O/-OH ratio of 1.3.

Lin et al. used WBPU as the film-forming material to prepare a water-based coating for ABS plastic, which had a smooth hand feel, soft luster, good scratch resistance, and excellent adhesion [15]. They also studied the effects of the types and amounts of defoamers, silicone coupling agents, elastic powders, wax dispersions, nitropyrazine crosslinking agents, thickeners, and other additives on the adhesion, water resistance, scratch resistance, and other properties of the coating. They prepared WBPU using aliphatic isocyanates and PC polyols as the main raw materials and added elastic powders (to improve scratch resistance), wetting agents, defoamers (to eliminate small and large bubbles), thickeners (to regulate viscosity), leveling agent, wax dispersion (for scratch resistance and soft feel), matting agent, silane coupling agents (to improve adhesion), nitropropidium crosslinking agents (to improve water resistance), film-forming agents, etc. The specific method was to first add water, defoamer, wetting agent, matte powder, and elastic powder in sequence. After the dispersion became uniform, WBPU, leveling agent, silane coupling agent, anti-freeze agent, film-forming agent, and wax dispersion were added in sequence. Then a thickener was added to regulate the viscosity. After being kept for 24 h, nitrogen and propidium crosslinking agents and water were added in sequence. Finally, spraying was performed

2–3 times on the ABS board cleaned with anhydrous ethanol. The coating was dried at room temperature for 2–3 h first, and then baked at 50 °C for 15–20 h. The final coating thickness was approximately 30 μ m. The results showed that the optimized defoamer was BYK024, the wetting agent was BYK190, the multifunctional additive was AMP95, the matting agent was N20, the elastic powder was P800T, the leveling agent was BYK348, the coupling agent was AC662, the anti-freeze was propylene glycol, the film-forming agent was TEXANOL ester alcohol, the wax dispersion was CERAFLOUR929, the thickner was TEGO3030, and the crosslinking agent was SaC100.

Shanghai Liangquan Packaging Materials Co., Ltd., Shanghai, China, first prepared the pre-coated hot melt adhesive or uncoated soft feel films and then laminated them on the surfaces of paper, plastic, and other materials to obtain the soft feel surfaces [39]. It could provide an alternative processing method to avoid direct spraying of soft-feeling materials. The Dutch company AkzoNobel (Amsterdam, Netherlands) developed DuraSilk UV coating in 2014, which could be applied to the surface of light-colored personal electronic consumer goods, giving them a softer texture [40]. It could be cured by UV at low temperatures, making it more energy-efficient, and the surface porosity was very low, having good stain resistance.

As can be seen from the above, there has been significant progress in the synthesis and preparation of soft feel materials represented by PU, SR, and PAA. But it can also be seen that these fields have not achieved breakthrough improvements in recent years. For example, most designs and synthesis of the PU soft feel materials have not deviated from the traditional ideas and processes. Therefore, it is necessary to obtain some inspiration from the development directions of relevant fields to boost innovation in this field. The related fields include, but are not limited to, advanced composites, electronic materials, and biomaterials.

4. The Application of Soft Feel Materials in Popular Fields Such as Mobile Phone Cases

Electronic products such as mobile phones, computers, and high-end consumer goods, including electronic cigarettes and cosmetics, have high economic added value, therefore requiring high-soft-feeling shells. Actually, the color and material of the mobile phone cases are almost equally important. The widely used materials for mobile phone cases currently include metal, rubber and plastic polymer materials, leather, and glass. Among them, common metal materials include aluminum alloy, titanium alloy, stainless steel, copper, etc.; engineering plastics include ABS, PC, polyphenylene oxide (PPO), etc.; and rubber elastomers include SR, thermoplastic polyurethane (TPU), etc. Besides, composite materials can be prepared by adding carbon fibers (CF), Kevlar fibers, and other materials to rubber and plastic polymer materials. Table 3 lists the related research on the soft feel of mobile phone cases.

References	Target Performances	Specific Strategies
[41]	Metallic texture	Depositing metal at the depth of the shell and attaching a matte metal texture baking paint to the surface.
[42]	Aesthetically pleasing	Baking paint, spraying various colors of paint, and sanding.
[43]	Keeping warm	Adding GF inside the shell to achieve thermal insulation and using SR heating plate supplied by an external electrical power.
[44]	Soft feel	Floating weaving Kevlar fiber for elastic polymer composite.

Table 3. Related research on the soft feel of mobile phone cases.

The main function of a mobile phone case is not only to protect the phone from scratches from hard objects and body wear but also to have functions such as aesthetics, anti-slip, anti-drop, waterproofing, and signal enhancement. Vivo Company, China, has achieved a metallic texture on PC phone cases using non-conductive electroplating spray

laser (NCL) technology [41]. The basic strategy is to deposit metal at the depth of the shell and attach a matte metal texture baking paint to the surface, giving it a texture that is extremely close to metal (aluminum alloy sandblasting, anodizing, and high gloss) and enhancing the smoothness of the grip.

Plastic and rubber phone cases can be injection molded, but their products are prone to defects such as under-injection, overflow, warping, shrinkage marks, fusion marks, cold material marks, bubbles, surface defects, etc. Therefore, it is necessary to regulate the characteristics of materials, the size and shape of molds, and the molding process conditions to improve the quality of products. Duan et al. proposed a solution to the problem of trapped air that was prone to occur during the injection molding process of mobile phone cases [45]. Han et al. also discussed the process and mold design of injection molding for mobile phone cases [46]. Shang et al. studied an automated injection molding mold for mobile phone cases, using injection pressure, time, and temperature as the influencing factors [47]. They simulated the fluid flow behavior inside the mold using the Moldflow software (Version 2021.0.1) to determine the optimal gate position. It simulated the pouring system and cooling circuit, analyzed the warping deformation, porosity, and fusion marks of the injection-molded parts, and ultimately determined the optimal processing technology combination scheme for the injection mold of the mobile phone case. The results indicated that the number of fusion marks produced by the two-point gate feeding was less than that of the four-point gate feeding, and uneven shrinkage was the biggest factor causing the overall deformation of injection-molded parts. They also provided the optimal process combination, including mold temperature, melt temperature, injection time, number of gates, layout of cooling channels, holding time, holding pressure, etc., which significantly reduced the amount of warping deformation.

The mobile phone case made of engineering plastics can be made more aesthetically pleasing through processes such as baking paint, spraying, and sanding, but poor thermal conductivity and heat dissipation are its main shortcomings [42]. Spraying various colors of paint on the phone case can change its color and texture, while in plastic and rubber phone cases, the spraying operation has the advantages of high production efficiency, a wide application range, and both manual and automated production. However, the automatic spraying operations require a dust-free workshop of millions to hundreds of levels, and the spraying equipment includes spray painting rooms, spray guns, curing furnaces, drying furnaces, workpiece conveying equipment, and waste gas treatment equipment. The highly dispersed paint mist and volatile organic solvents generated in the automatic spraying operations not only pollute the environment and are not conducive to human health, but also waste the coating materials and cause some economic losses [48].

In response to the problem of weakened performance of lithium-ion batteries for mobile phones in extremely cold areas, which generally leads to poor phone usage, Wei et al. designed a phone case with insulation and heating functions that included butyl rubber, ABS plastic, a leather shell, and an SR heating plate [43]. Glass fiber (GF) was added inside the shell to achieve anti-slip, anti-drop, and thermal insulation effects, as well as good tactile sensation. The SR heating plate integrated a temperature control module, which was heated by an external power supply (such as a power bank) through resistance wires or other heating elements (as shown in Figure 3). Tests showed that the phone case could ensure the normal operation of the mobile phone at low temperatures of -20 °C.

Currently, the most eye-catching, super-soft-feeling mobile phone case is made of Kevlar fiber woven composite material, which has been highly praised by a large number of users. Among them, in response to the traditional weaving method of Kevlar fiber, which only has two-color flat or diagonal weaving and relatively single patterns and colors, Shenzhen Zero One Innovation Technology Co., Ltd., Shenzhen, China, developed a floating weaving technology called PitakaTM in October 2021, achieving multiple patterns, colors, and three-dimensional sense, thereby providing a carved visual and touch experience for this type of mobile phone case in terms of appearance and touch [44]. Specifically, this process involved adjusting the alternating order of warp and weft for different primary

color Kevlar fibers, allowing the fabric to produce two or more different weaving interlacing and three-dimensional arrangements on the same plane. Figure 4 shows a physical photo of the PitakaTM 1500 D Kevlar fiber polymer composite phone case. It not only has strong impact resistance but is also of light weight (typical thickness of about 0.95 mm, weight of about 17.3 g), anti-slip, anti-fouling (without leaving fingerprints), good heat dissipation, and excellent soft feel.



Figure 3. Schematic diagram of the structure of a mobile phone case with thermal insulation and heating function (1: case, 2: heating plate, 3: charging plug, 4: wire, 5: external power supply) (modified from Reference [43] with permission).



Figure 4. PitakaTM 1500 D Kevlar fiber polymer composite mobile phone case produced by Shenzhen Zero One Innovation Technology Co., Ltd., China.

The emergence of Kevlar fiber composite mobile phone cases not only validates many aspects of the formation mechanism of soft feel mentioned earlier, but also provides a good reference for the design and preparation of new soft feel materials. The design concept of "flexible under small deformation and tough under large deformation" in terms of mechanical properties also provides a good strategy for the application of rubber and plastic-based polymer micro- and nano-composites in soft-feel materials. At the same time, other important surface properties of these products, such as heat dissipation performance, anti-fouling performance, etc., are also important considerations that we need to focus on when designing the soft-feel materials. Concerning the adhesion of soft-feel materials to the plastic substrate, chemical reactions during coating formation definitely provide high bonding strength. But even without the chemical reaction, most soft-feel coatings can still adhere strongly to the plastic substrate through van der Waals forces and/or hydrogen bonding.

5. Discussion and Outlook

According to the above overview and earlier references (as shown in Figure S1 and Table S1 in the Supplementary Materials) [49–54], we can clearly see that the application of soft-feel materials is very important for improving the quality and price level of hard plastic products, so it is necessary to continue the in-depth research and development. However, there are still many questions worth further exploring regarding the psychophysical mechanisms underlying the generation of soft feel, which are important for guiding the selection, design, and preparation of soft feel materials. Considering that the chemical composition, synthesis methods, and selection of additives for PU soft feel materials have become relatively mature, significant breakthroughs are urgently needed in the near future. Especially for high-value products such as mobile phone cases, there are higher requirements for soft-feel materials, requiring revolutionary breakthroughs in the design concepts and implementation strategies.

In terms of the future development directions of soft-feel materials, the following several aspects are definitely worth exploring in depth: First, compared with the traditional systems, the solvent-based single-component system, the water-based system, and the UV curing system all have their own characteristics that meet the requirements of the times, so they are worth expanding and optimizing. Secondly, the use of multiple material composites to achieve synergistic effects is the material foundation that meets the requirements of high-quality products for light weight, high strength, high thermal conductivity, fast heat dissipation, self-cleaning, etc. Last but not least, simultaneously meeting the basic requirements such as environmental protection and affordability, as well as possessing anti-fingerprint and anti-static properties, is an urgent requirement for the multifunctionality of soft-feel materials.

6. Conclusions

Considering that the soft feel material (mainly PU, SR, and PAA, etc.) coatings can overcome the drawbacks of the cold, hard, and bright surfaces of common plastic products such as ABS, PC, and PP to achieve warm, soft, and matte effects, thus greatly improving their quality and price level, and there is still a lack of in-depth overview on the design philosophy and preparation strategies of soft feel materials, this review has started from the mechanism of producing soft feel, then systematically explored the application of soft feel materials, and finally systematically overviewed the research and development progress of the soft feel materials with a focus on PU. It has been concluded that both in-depth understanding of the psychophysical mechanisms of soft feel and further development of the design, preparation, characterization, and application of soft feel materials are needed. High-value products have higher requirements for soft-feel materials, so revolutionary breakthroughs in design concepts and implementation strategies such as surface engineering and the combination of multiple and hybrid materials are strongly expected.

Supplementary Materials: The following supporting information can be downloaded at: https: //www.mdpi.com/article/10.3390/coatings14060748/s1, Figure S1. Single cavity injection molding process: injection of thermoplastic (a), injection of coating after opening the mold (b), and curing of coating after closing the mold (c) (modified from reference [S6] with permission). Table S1. The (optimized) formula of PU soft feel materials (sorted by the publication date of literature). References [49–54] are cited in the supplementary materials.

Funding: This research received no external funding.

Data Availability Statement: Data are contained within the article and Supplementary Materials.

Conflicts of Interest: Author Lanlan Zhang was employed by the company Shenzhen ShineCMF Advanced Materials Co., Ltd. The remaining authors declare that the research was conducted in the

absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

List of Abbreviations

ABS	acrylonitrile butadiene styrene copolymer
AFM	atomic force microscope
BDO	butanediol
BOPP	biaxially oriented polypropylene
CF	carbon fiber
DBTDL	dibutyltin dilaurate
DMPA	dihydroxymethylpropionic acid
ESM	eggshell membrane
FTIR	Fourier transform infrared spectroscopy
GF	glass fiber
HDI	hexamethylene diisocyanate
HTS	high tactile sensation
IPDI	isophorone diisocyanate
LTS	low tactile sensation
NCL	non-conductive electroplating spray laser engraving
PAA	polyacrylic acid
PC	polycarbonate
PDMS	polydimethylsiloxane
PETA	pentaerythritol triacrylate
PP	polypropylene
PPO	polyphenylene oxide
PTMG	polytetrahydrofuran ether glycol
PU	polyurethane
SR	silicone rubber
TEA	triethylamine
TPM	tribological probe microscope
TPO	thermoplastic polyolefin
TPU	thermoplastic polyurethane
UV	ultraviolet light
VOC	volatile organic compounds
WBPU	waterborne polyurethane

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Nu Yan^{1,*}, Ziyun Zhu¹, Yuchuan Cheng¹, Fang Liu¹, Min Shen¹ and Hongjun Li^{1,2}

- ¹ School of Mechanical Engineering and Automation, Wuhan Textile University, Wuhan 430200, China; 18327585117@163.com (Z.Z.)
- ² Hubei Engineering Research Center for Intelligent Assembly of Industrial Detonators, Wuhan 430200, China
- * Correspondence: yannu@wtu.edu.cn

Abstract: In order to enhance the surface properties of GCr15 bearing steel, a TiAlCN coating with a low friction coefficient, high hardness, and excellent adhesion was fabricated. The TiAlCN multilayer coating was deposited onto the GCr15 bearing steel surface using magnetron sputtering technology, and optimal coating parameters were achieved by adjusting the number of layers, sputtering power of the graphite target, and coating duration. The experimental results showed that adding Cr/CrN as a transition layer between GCr15 bearing steel and TiAlCN significantly improved multiple properties of the coating. Adding carbon atoms caused TiAlN to dissolve into a TiAlCN structure, enhancing multiple properties of the coating. With the increase in the sputtering power of the graphite target material, the hardness, friction, and wear performance of the coating showed a trend of first increasing and then decreasing. The hardness of the coating gradually increased with time, and the friction coefficient and wear amount first decreased and then increased. When the sputtering power of the graphite target material was 100 W and the coating time was 4800 s, the coating performance was optimal. The hardness was 876 HV, the friction coefficient was 0.42, the wear amount was 1 × 10⁻⁴ g, and the wear rate was 2.8×10^{-6} g/m·N under optimal process parameter conditions.

Keywords: magnetron sputtering; Cr/CrN/TiAlCN composite coating; sputtering power; coating time; friction coefficient

1. Introduction

Bearing steel has excellent properties, such as high strength, high hardness, good wear resistance, and corrosion resistance, and it is an important foundational material in the mechanical manufacturing industry [1]. With the increasingly harsh service environment and diverse and complex operating conditions of bearings, economic losses and engineering accidents caused by damage and failure of bearing steel components are also increasing [2]. Improving the service life and performance of bearing steel mechanical components is becoming increasingly important. Surface treatment is an effective way of improving the performance and extending the lifespan [3]. For medium to large-sized bearing steel components, traditional heat treatment is the most prevalent method for enhancing performance. For small-sized bearing steel components, surface coating technology offers greater convenience and superior effectiveness. Coatings prepared with the physical vapor deposition (PVD) method not only have excellent wear resistance [4] and corrosion resistance [5] but also have many advantages such as low deposition temperature, no pollution, a wide selection of coating materials, and good surface roughness. The most significant advantage is the ability to apply the PVD technique to coat various types of substrates, providing a wide range of coating thicknesses [6]. This is expected to become one of the preferred methods for preparing high-quality coatings on bearing steel surfaces in the future.

As the earliest industrial PVD coating, the TiN coating has been widely used in various fields due to its good hardness and wear resistance [7]. With the development of industrial

Citation: Yan, N.; Zhu, Z.; Cheng, Y.; Liu, F.; Shen, M.; Li, H. Preparation and Performance of a Cr/CrN/ TiAlCN Composite Coating on a GCr15 Bearing Steel Surface. *Coatings* **2024**, *14*, 782. https://doi.org/ 10.3390/coatings14070782

Academic Editors: Ricardo Lopez Anton, Jose Maria De Teresa and Sion Federico Olive Méndez

Received: 22 May 2024 Revised: 14 June 2024 Accepted: 18 June 2024 Published: 21 June 2024



Copyright: © 2024 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). production towards higher precision and speed, the thermal stability of coatings has an increasingly important impact on their service performance and service life. Scholars have attempted to add Al to TiN coatings to form a TiAlN coating system with improved thermal stability, high-temperature oxidation resistance, and heat fatigue resistance [8]. TiAlCN coatings are a new type of quaternary coating developed on the basis of ternary TiAlN coatings, and they have better plasticity, toughness, and friction and wear resistance than those of TiAlN coatings [9]. Wang et al. [10] prepared Al₂O₃-Ag-Cu-Ti composite coatings on GCr15 bearing steel using plasma spraying technology. They found that coatings deposited in a vacuum chamber at 900 °C for 10 min exhibited excellent bonding strength and toughness. Ke L. et al. [11] prepared a superhard TiAlCN coating with a hardness of up to 42.6 GPa on the surface of Ti-6Al-4V alloy using multi-arc ion plating technology. Chen S.N. et al. [12] used magnetic filtration technology to prepare TiAlCN/TiAlN/TiAl composite coatings on 304 stainless steel and investigated the effect of the carbon content on the coating performance. However, the PVD technologies used by the aforementioned scholars, such as arc ion plating and thermal spraying, are prone to defects such as particles, protrusions, and pits on the coating surface, due to the high energy and temperature generated during the preparation process, which affect the quality of the film. Compared with other methods, magnetron sputtering technology has the advantages of high speed, low temperature, low damage, and uniform coating; thus, it can effectively solve these defect problems. Coating surface treatment technology can significantly improve the performance of materials, and the reasonable design of multi-layer composite coatings in coating surface treatments is expected to provide further modifications [13–16]. The matrix material used in this study was GCr15 bearing steel, which is the most commonly used in engineering practice. Due to its good compatibility with bearing steel matrices, CrN coatings have been widely used as a transition layer in the surface treatment of bearing steel components. The research results indicate that depositing CrN on the surface of GCr15 bearing steel components can provide a good bonding effect between the coating and the substrate [17,18].

In order to improve the service performance of GCr15 bearing steel, considering the advantages of magnetron sputtering technology in thin-film formation and the excellent performance characteristics of TiAlCN thin films coupled with the lack of systematic research on TiAlCN coatings and their application on the surface of GCr15 bearing steel, this study adopted magnetron sputtering technology to prepare Cr/CrN/TiAlCN composite coatings on GCr15 bearing steel, described the innovative design of Cr/CrN as the transition layer of the coating, and explored the influence of multiple nano-layers on the microstructure and properties of the coating. In order to obtain a better composite coating, the effects of the carbon content and coating time on the coating were studied.

2. Materials and Methods

2.1. Coating Preparation

The experimental equipment used was an MSP-620 fully automatic magnetron sputtering coating machine manufactured by Beijing Jinsheng Micro Nano Technology Co., Ltd. (Beijing, China) The substrate was GCr15 bearing steel with a size of Φ 15 × 5 mm. Table 1 shows the chemical composition of GCr15 bearing steel; it was polished from coarse to fine and then ultrasonically cleaned with acetone and anhydrous ethanol solution in sequence. The target materials included high-purity Cr targets, high-purity graphite targets, and TiAl alloy targets (Ti.at%:Al.at% = 1:1). RF power was used to sputter the graphite targets, while DC power was used to sputter the Cr targets and TiAl targets.

Table 1. Chemical composition of GCr15 bearing steel.

Element	Cr	С	Mn	Si	Р	S
Content (wt.%)	1.30-1.65	0.95-1.05	0.20-0.40	0.15-0.35	≤ 0.027	≤ 0.020

Firstly, a pure Cr layer was deposited on the substrate surface for 5 min; then, N₂ was introduced for 10 min so that a CrN transition layer would be deposited, and finally, TiAlCN coatings were deposited with different graphite target sputtering powers and coating times. Basic process parameters: The background vacuum degree was 8×10^{-4} Pa, the working pressure was 1 Pa, the TiAl target power was 110 W, the argon flow rate was 60 sccm, and the nitrogen flow rate was 50 sccm. The specific experimental process parameters are shown in Table 2.

Table 2. Process parameters.

Process Parameters						
Coating	Cr	CrN	TiAlCN			
Background vacuum degree (GPa)	$8 imes 10^{-4}$	$8 imes 10^{-4}$	$8 imes 10^{-4}$			
Working air pressure (Pa)	1	1	1			
Coating power (W)	Cr:100	Cr:100	TiAl: 110 Graphite: 0-120			
Coating time (s)	300	600	1200, 2400, 3600, 4800, 6000			
Ar_2 flow (sccm)	90	60	60			
N ₂ flow (sccm)	0	50	50			

In order to obtain better coating preparation process parameters and explore the effects of multiple layers, the graphite target sputtering power, and the coating time on the coating performance, this study adopted the controlled variable method for the experimental design. The experimental plan is shown in Table 3.

Sample	Sample Graphite Target Power (W)		Number of Layers
S0	0	0	0
S1	100	6000	1
S2	100	6000	3
S3	0	6000	3
S4	30	6000	3
S5	50	6000	3
S6	80	6000	3
S7	120	6000	3
S8	100	1200	3
S9	100	2400	3
S10	100	3600	3
S11	100	4800	3

Table 3. Experimental plan.

2.2. Characterization of the Coating Structure

The morphology of the coating surface and cross-section were characterized using an OLYMPUS-DSX510 metallographic optical microscope (Tokyo, Japan) and a JSM-7800 thermal field emission scanning electron microscope (Tokyo, Japan) (equipped with Oxford EDS probe). The types and relative contents of the coating elements were analyzed using EDS probes equipped with an SEM. The analysis of the phase composition and crystal structure of the coating was conducted using an Empyrean X-ray diffractometer (Almelo, Holland) with Cu K- α , a scanning angle of 20–90°, and the scanning mode set to 20 continuous scanning.

2.3. Characterization of the Coatings' Mechanical Properties

An HBE-3000A adhesion tester (Shanghai, China) was used to test the adhesion performance of the coating film substrate, and the pore indentation morphology obtained with the tester was photographed using an optical microscope. The obtained images were compared with a standard reference card (as shown in Figure 1), and the adhesion force of the film substrate was analyzed based on the cracks and peeling of the coating at the edge



of the indentation. Levels 1–4 were in the acceptable range of failures, and levels 5–6 were in the unacceptable range of failures.

Figure 1. Diagram of the standard indentation card.

The HV1000 microhardness tester (Shanghai, China) was used to measure the hardness of the coating. In this experiment, the load was set to 200 g, and the retention time was 10 s. Six points were measured at different positions on the sample surface, and the average value was calculated.

2.4. Friction and Wear Experiments

An SPM-9700 atomic force microscope was used to analyze the three-dimensional morphology and surface roughness of the coating (Tokyo, Japan). Before scanning, the sample was cut into thin slices with a diameter of 15 mm and a height of 1 mm using a wire-cutting machine. The scanning area was set to $200 \times 200 \mu$ m, and the scanning speed was set to 200 lines per minute.

Friction and wear experiments were conducted using an MFT-5000 multifunctional friction (Rtec Instruments, San Jose, CA, USA) and wear testing machine. The experiment used Si_3N_4 balls (with a diameter of 5 mm) as grinding balls, and they moved in a linear reciprocating motion. The load force was set to 1 N, the one-way travel was set to 5 mm, the frequency was adjusted to 2 Hz, and the grinding time was 30 min. The principle of friction between discs was used to obtain the curve of the friction coefficient over time. The sample quality before and after the experiment was recorded to determine the amount of wear. The wear rate was calculated according to Formula (1) [6].

$$N = \frac{m}{S \cdot L} \tag{1}$$

In the formula, W is the wear rate, *m* is the amount of wear, *S* is the loading force, and *L* is the total sliding distance.

3. Results and Discussion

3.1. Morphology and Structure of the Coatings

In Figure 2d,f,i–l, it can be seen that after being magnified 1000 times, there were randomly distributed small defects, such as pits, particles, and pinholes, of different shapes and sizes on the surface of the coating. This was because during the DC sputtering process, the insulation layer on the target surface was continuously sputtered down by the accumulated positive charge, which could not react with ions in the plasma while flying towards the substrate, thus forming defects on the substrate surface [19]. The remaining coating surface had no obvious defects. Meanwhile, as shown in Figure 2g–l, it can be seen that as the carbon content increased, there were more small particles and pits on the surface of the coating. However, overall, the coating surface was smooth, dense, and flat, with good film quality, which proved that the surface morphology of the coating prepared on

GCr15 bearing steel based on the magnetron sputtering technology studied here was good, effectively improving the surface defect problems that cannot be avoided with multi-arc ion plating, thermal spraying, and other traditional surface treatment technologies.

The relative elemental contents of the coating were measured using EDS, and the results are shown in Table 4. As the power to the graphite target rises and the coating duration extends, the carbon-to-nitrogen ratio in the coating progressively increases. This is due to the higher power elevating the energy of carbon within the target material. Additionally, prolonged coating times result in more carbon atoms being sputtered, leading to increased deposition on the substrate surface and consequently a higher carbon content in the coating. Concurrently, an excess of carbon atoms replaces nitrogen atoms, creating TiAlCN structures on the coating surface and elevating the carbon-to-nitrogen ratio.

Sample	Cr/at.%	Ti/at.%	Al/at.%	C/at.%	N/at.%
S1	0	18.04	21.73	12.03	48.20
S2	14.86	15.30	19.38	11.37	39.09
S3	17.32	17.61	21.74	0	45.33
S4	16.95	18.37	19.09	4.85	42.74
S5	15.59	15.01	20.52	6.97	41.91
S6	14.53	16.31	19.94	9.76	39.46
S7	15.20	13.86	17.09	13.03	38.82
S8	32.83	5.27	7.28	8.25	46.37
S9	25.46	7.09	9.93	9.93	47.59
S10	21.09	9.91	12.17	9.02	47.89
S11	17.26	12.93	13.88	10.16	45.77

Table 4. Table of the relative elemental contents of the coatings.



Figure 2. Cont.



Figure 2. Morphology of the coating as determined with an SEM: (a) S1; (b) S8; (c) S9; (d) S10; (e) S11; (f) S2; (g) S1; (h) S3; (i) S4; (j) S5; (k) S2; (l) S6.

Figure 3 shows the cross-sectional morphology of the coatings, where a represents the TiAlCN single-layer coating sample S1, b represents the Cr/CrN/TiAlCN multi-layer coating sample S2 at a graphite target power of 100 W, and c represents the multi-layer coating sample S4 at a graphite target power of 30 W. As shown in the figure, the cross-section of the coating was continuous and uniform, with no obvious defects, and it had a thickness of about 1.8 μ m. In the figure, for b and c, it can be clearly seen that the coating had a two-layer structure. It was observed that there was a clear boundary between the TiAlCN layer and the Cr/CrN layer at the top layer, and the boundary between the Cr and CrN layers was not obvious due to the thin coating. When the carbon content was low at 4.85%, the columnar crystal structure of the TiAlCN layer was coarse. When the carbon content reached 11.37% (sample S2), the columnar crystal structure of the TiAlCN layer was weakened, and the microstructure became dense. This is due to the increased presence of the C element, which hinders grain growth and leads to grain refinement and reduced cylinder growth [12].

Figure 4 shows the X-ray diffraction patterns of the coatings. As shown in Figure 4a, except for the matrix diffraction peaks at around 44° and 64°, the coating mainly had two diffraction peaks. When the carbon content in Figure 4b was 0, the coating had a face-centered cubic structure and grew exponentially along multiple crystal faces. The diffraction peaks corresponding to the 37.6° and 77.8° accessories were (Ti, Al) (C, N) (111) and (311), respectively. When the graphite target material started sputtering, the addition of C replaced some N atoms, causing the diffraction peak of the coating to shift to the left. Meanwhile, with the increase in the C content and the extension of the coating continuously increased, and the peak intensity of the (111) crystal plane was always higher than that of

the (311) crystal plane. As can be seen from Figure 4c, the diffraction peak of the coating shifted as the coating time was extended, because more and more C atoms replaced N atoms in the coating as the coating time was extended, resulting in a leftward shift. This was because the (111) crystal plane usually had the smallest growth surface energy, and the crystal grew towards the crystal plane with a lower surface energy. Therefore, the coating exhibited a preferred orientation of the (111) crystal plane [20].



Figure 3. Cross-sectional morphology of the coating: (a) cross-sectional view of the single-layer coating (S1); (b) cross-sectional view of a multi-layer coating (S2); (c) cross-sectional view of a multi-layer coating (S4).



Figure 4. XRD patterns of the coatings: (a) number of layers; (b) graphite target power; (c) coating time.

3.2. Mechanical Properties of the Coatings

Figure 5 shows an indentation diagram of the bonding performance of the coatings. There was a large amount of peeling at the edge of the indentation of the single-layer TiAlCN coating, as shown in Figure 5a. The card indicated level 3 failure, and its bonding performance was average. Under the same preparation conditions, the multi-layer Cr/CrN/TiAlCN composite coating had only slight cracks and no peeling at the edge of the indentation, indicating level 1 failure with good bonding performance. This was because the crystal structure of GCr15 bearing steel is a body-centered cubic system, which is composed of iron atoms and chromium atoms in the face-centered cubic, while, as shown in Figure 4, the crystal structure of the TiAlCN coating was mainly composed of face-centered cubic fcc-(Ti, Al) (C, N). The crystal structures of the two materials were different, and there was a significant difference in the atomic size, which could lead to lattice mismatch and unsynchronized crystal morphologies, resulting in poor membrane substrate adhesion. The transition layer could provide a buffering effect between the two, and the lattice structure transitioned relatively smoothly to reduce lattice mismatch and improve the compatibility of the two materials, thereby improving the bonding performance between the coating and the substrate [21]. The bonding performance is the most basic criterion for measuring whether a coating can be applied to a substrate. Only with a good bonding performance can the preparation of a coating have more practical significance. The innovative use of Cr/CrN as the transition layer between GCr15 bearing steel and the TiAlCN coating in this project improved the film-based adhesion, laying the foundation for the application and development of TiAlCN coatings deposited on GCr15 bearing steel in the future.



Figure 5. Indentation diagram of the coatings: (a) S1; (b) S8; (c) S9; (d) S10; (e) S11; (f) S2; (g) S3; (h) S4; (i) S5; (j) S6; (k) S2; (l) S7.

In Figure 5b,c, it can be seen that the peeling and cracking around the coating pits were obvious, indicating level 3 and level 4 peeling. This was because, in the case of a short coating time, the coating preparation was uneven, and there were more crystal defects at the bonding interface, resulting in a weak bonding force [22]. With the continuous increase in the coating time, the adhesion of the coating continued to improve, and the number of cracks at the edge of the indentation decreased, as shown in Figure 5d,e.

Figure 5g,h show the surface indentation morphologies of the coating when the graphite target power is 0 W and 50 W, respectively. It can be seen that when carbon was added, the morphology around the coating indentation was improved, and the bonding

performance of the coating was enhanced. As the carbon content increased, as shown in Figure 5j–l, there were only small amounts of peeling and micro-cracks in the coating. With its level 1 and 2 peeling, the coating had excellent bonding performance. However, when the sputtering power of the target material exceeded a certain value, the energy of the ionized particles increased, leading to an increase in the substrate temperature, an increase in lattice defects in the coating, relaxation of internal stress, decreased adhesion, and decreased bonding performance [23], as shown in Figure 5g.

Figure 6 presents a schematic diagram of the microhardness of the coatings. As shown in Figure 6a, the hardness of the samples after no coating, single-layer coating, and multilayer coating increased linearly. The deposition strengthening layer of the TiAlCN film significantly improved the hardness of the substrate, and adding Cr/CrN as a transition layer on this basis further improved the hardness of the coating. Correspondingly, adding a transition layer in the previous section improved the bonding performance of the coating, and the strength of the coating's resistance to external forces was greater, resulting in higher hardness.



Figure 6. Microhardness of the coatings: (a) number of layers; (b) graphite target power; (c) coating time.

As the graphite target power increased, the coating hardness first increased and then decreased, as shown in Figure 6b. This was because TiAlN solidly dissolved into TiAlCN, forming an elastic strain field centered on C atoms. When dislocations moved near C atoms, the resistance increased, thus strengthening the thin film. Therefore, the hardness value of the TiAlCN coating was greater than that of the TiAlN coating. As the C content increased, more C elements were dissolved in TiAlN, strengthening and enhancing the hardness of the film. The microhardness of the TiAlCN film reached a maximum of 876 HV when the graphite target power was 100 W. However, when the sputtering power was too high, the surface temperature of the coating in the same section was too high, which led to a decrease in the bonding performance and thus affected the hardness of the coating.

As the coating time increased, the hardness of the coating continued to increase, as shown in Figure 6c. This was because the increase in sputtering time led to an increase in the deposition rate of the coating. Harder TiAICN coatings were deposited on the substrate, and the thickness of the coating also increased, improving the hardness of the coating.

3.3. Friction and Wear Performance of the Coatings

Figure 7 shows a friction factor diagram of the coatings. In Figure 8a, it can be seen that the effect of using multiple layers on the friction coefficient of the coating was the same as that of hardness. Figure 8b reflects the effect of the graphite target power on the friction factor of the coating, indicating that the friction coefficient of the coating first decreased and then increased with the increase in the power. Figure 8c reflects the effect of the coating time on the friction coefficient of the coating. As the sputtering time increased, the friction coefficient of the coating time was 4800 s, the minimum friction coefficient of sample S11 was 0.42. When the sputtering time was too long, the structure of the coating could change, leading to surface oxidation or precipitation of other phases, thereby causing the friction coefficient to rise again. At the same time, if the coating increased, and the friction and wear coefficients of the coating also increased. In summary, the friction coefficient of the coating first decreased and then increased with the extension of the coating time. At 4800 s, the friction coefficients of the coating time. At 4800 s, the friction coefficient was the smallest.



Figure 7. Friction coefficient diagram of the coatings: (a) number of layers; (b) graphite target power; (c) coating time.

Table 5 shows the friction parameters of the coatings. Figure 8 shows the wear amount and wear rate of the coatings. As shown in the figure, under the same friction conditions, the wear of sample S1 with the single-layer TiAlCN coating decreased by 1.1×10^{-4} g compared with that of the uncoated sample S0, and the wear rate decreased by 30.1%. The wear of sample S2 with the multi-layer Cr/CrN/TiAlCN composite coating decreased by 2.4×10^{-4} g compared with that of the uncoated sample, and the wear rate decreased by 2.4×10^{-4} g compared with that of the uncoated sample, and the wear rate decreased by 2.4×10^{-4} g compared with that of the uncoated sample, and the wear rate decreased by 2.4×10^{-4} g compared with that of the uncoated sample, and the wear rate decreased by 2.4×10^{-4} g compared with that of the uncoated sample, and the wear rate decreased by 2.4×10^{-4} g compared with that of the uncoated sample, and the wear rate decreased by 2.4×10^{-4} g compared with that of the uncoated sample, and the wear rate decreased by 2.4×10^{-4} g compared with that of the uncoated sample, and the wear rate decreased by 2.4×10^{-4} g compared with that of the uncoated sample, and the wear rate decreased by 2.4×10^{-4} g compared with that of the uncoated sample, and the wear rate decreased by 2.4×10^{-4} g compared with that of the uncoated sample.

68%. This proved that TiAlCN is an excellent wear-resistant and wear-reducing coating for GCr15 bearing steel. Meanwhile, in the same friction environment, adding Cr/CrN as a transition layer between GCr15 bearing steel and the TiAlCN coating significantly reduced the wear. Placing the Cr/CrN/TiAlCN composite coating on GCr15 bearing steel was the best coating design solution.



Figure 8. Schematic diagram of the wear amount and wear rate of the coatings: (a) number of layers; (b) graphite target power; (c) coating time.

Table 5. Friction p	parameters of	the coatings.
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Sample	m1 (g)	m2 (g)	M (10 ⁻⁴ g)	L (m)	S (N)	W (10 ⁻⁶ g/N.m)	Average Coefficient of Friction
S0	36.08332	36.08297	3.5	36	1	9.7	0.78
S1	36.18471	36.18447	2.4	36	1	6.7	0.65
S2	36.17425	36.17414	1.1	36	1	3.1	0.45
S3	36.16532	36.16503	2.9	36	1	8.1	0.69
S4	36.17406	36.17380	2.6	36	1	7.2	0.62
S5	36.17517	36.17495	2.2	36	1	6.1	0.58
S6	36.05428	36.17495	1.6	36	1	4.4	0.52
S7	36.15085	36.15072	1.3	36	1	3.6	0.5
S8	36.23594	36.23543	4.1	36	1	11.4	0.79
S9	36.20076	36.20051	2.5	36	1	6.9	0.75
S10	36.17523	36.17509	1.4	36	1	3.9	0.62
S11	36.15367	36.15357	1.0	36	1	2.8	0.42

The wear amount of the TiAlN coating deposited on GCr15 bearing steel was reduced by 0.6×10^{-4} g when compared with that of the uncoated bearing steel, and the wear rate was reduced by 16.5%, indicating that the TiAlN coating also had the function of wear resistance and wear reduction. When the carbon content in the coating was 4.85%, compared with that of the TiAlN coating, the wear amount was reduced by 0.3×10^{-4} g,

and the wear rate was reduced by 11.1%. At the same time, the relationship between the friction coefficient, wear amount, and wear rate of the coating and the carbon content was the same as the relationship between the hardness and carbon content, which first decreased and then increased with the increase in the carbon content.

When the coating time was 1200 s, the wear amount of the coating was 4.1 g and the wear rate was 11.4×10^{-6} g/m·N, which were greater than the wear amount and wear rate of the uncoated bearing steel. If the coating time was too short, the coating appeared to undergo block-like detachment during friction and wear, and the wear amount increased. As the coating time increased, the wear amount, wear rate, and friction coefficient of the coating showed the same trend. When the coating time was 4800 s, the friction performance of the coating was optimal.

4. Conclusions

The main conclusions obtained through this experimental research were as follows.

- This study innovatively added Cr/CrN as a transition layer in GCr15 bearing steel and TiAlCN to provide a buffering effect between the substrate and the coating, significantly improving the coating performance.
- (2) When the graphite target power was 0, the TiAlN coating showed a clear columnar crystal structure. After adding carbon atoms, the columnar crystal structure was weakened, and carbon atoms replaced nitrogen atoms, enhancing the mechanical and friction wear properties of the coating.
- (3) As the coating time increased, the roughness of the coating continuously changed, and the bonding performance and hardness continued to improve. The friction coefficient and wear parameters showed a trend of first decreasing and then increasing.
- (4) The optimal process parameters were a graphite target sputtering power of 100 W and a coating time of 4800 s. Compared with the uncoated GCr15 bearing steel, the coating hardness increased by two times after coating, the friction coefficient decreased by 0.36, the wear amount decreased by 2.5 × 10⁻⁴ g, and the wear rate decreased by 71%.

The results of this research provide an important basis for optimizing the process parameters of magnetron sputtering treatments on the surface of bearing steel, improving the service performance of GCr15 bearing steel components, and extending their service life, thereby saving costs in industrial production and creating greater economic value.

Author Contributions: Conceptualization, NY., F.L. and H.L.; Methodology, N.Y., Z.Z., M.S. and H.L.; Validation, Z.Z. and Y.C.; Data curation, Z.Z.; Writing—original draft, Z.Z.; Writing—review & editing, N.Y. and Z.Z. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Data are contained within the article.

Conflicts of Interest: The authors declare no conflicts of interest.

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Article



Transport Behavior of Paranitroaniline through a Flat-Sheet Supported Liquid Membrane Using Tributylphosphate as a Carrier

Azizah Algreiby ^{1,*}, Lama Alharbi ¹, Noura Kouki ¹, Haja Tar ¹, Abrar Alnafisah ¹ and Lotfi Béji ²

- ¹ Department of Chemistry, College of Science, Qassim University, Buraydah 52571, Saudi Arabia; n.kouki@qu.edu.sa (N.K.)
- ² Department of Physics, College of Science, Qassim University, Buraydah 52571, Saudi Arabia
- * Correspondence: grieby@qu.edu.sa; Tel.: +966-533-010-572

Abstract: 4-Nitroaniline (PNA) is a toxic organic compound commonly found in wastewater, posing significant environmental concerns due to its toxicity and potential carcinogenicity. In this study, the recovery of PNA from aqueous solutions was investigated using a supported liquid membrane (SLM). The membrane, which consists of polypropylene Celgard 2500 (PP-Celg), was embedded with the extractant tributyl phosphate (TBP). Various factors influencing the efficiency of PNA transportation were studied, including the concentration of PNA in the source phase, pH of the source phase, NaOH concentration in the receiving phase, and choice of stripping agents. Optimal conditions for the experiment were determined to be a source phase PNA concentration of 20 ppm at pH 7, distilled water as the receiving phase, TBP as the carrier in the organic phase, and a transport time of 8 h. The extraction process was conducted under ambient temperature and pressure conditions, yielding results indicative of a first-order linearized reaction. Additionally, membrane stability and liquid membrane loss were evaluated.

Keywords: 4-Nitroaniline (PNA); supported liquid membrane (SLM); polypropylene Celgard 2500 (PP-Celg); tributyl phosphate (TBP); separation

1. Introduction

PNA is an organic compound that is an intermediate in synthesizing pharmaceuticals, drugs, gasoline, and dyes. It is a solid powder with a bright yellow color and a slight ammonia-like odor. Due to its classification as a toxic compound particular handling, use, and disposal procedures must be in place for this substance [1,2]. It belongs to refractory pollutants commonly found in wastewater and, because of their toxicity and probable carcinogenic consequences, pose a serious threat to the environment.

The release of PNA during its production and utilization poses a serious environmental problem. It may cause long-term adverse effects in terms of hepatoxicity, splenotoxicity, and nephrotoxicity [3,4]. According to the United States Environmental Protection Agency (UEPA), this material is the top contaminant in water because of its toxicity, carcinogenicity, and mutagenicity. PNA metabolites are nonbiodegradable or slowly degradable and have varying toxicities to aquatic life and organisms. PNA is resistant to chemical and biological oxidation degradation due to a nitro group linked to the aromatic ring [5].

Treating wastewater containing PNA prevents environmental pollution and protects human health. Various methods have been developed for PNA removal. Wastewater containing PNA can be treated using physicochemical methods, such as adsorption, photodegradation, biodecomposition, and electrochemical treatment. Adsorption is the most effective method because it is easy to use, even when treating enormous amounts of wastewater. But adsorption methods for treating wastewater suffer from issues like high reagent

Citation: Algreiby, A.; Alharbi, L.; Kouki, N.; Tar, H.; Alnafisah, A.; Béji, L. Transport Behavior of Paranitroaniline through a Flat-Sheet Supported Liquid Membrane Using Tributylphosphate as a Carrier. *Colloids Interfaces* **2024**, *8*, 49. https:// doi.org/10.3390/colloids8050049

Academic Editors: Ricardo Lopez Anton, Jose Maria De Teresa, Sion Federico Olive Méndez and Wuge Briscoe

Received: 9 July 2024 Revised: 22 August 2024 Accepted: 30 August 2024 Published: 4 September 2024



Copyright: © 2024 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). consumption (e.g., adsorbents and catalysts) [6–8]. Also, a bioreactor widely used worldwide in methods for wastewater treatment is the biological aerated filter (BAF). Through carrier filtration and biodegradation, BAF can eliminate contaminants. BAF, a biofiltrationbased wastewater treatment technique, has the features of high biomass retention, toxin tolerance, superior removal efficiency, and slurry separation [9,10]. However, bubble aeration in a BAF may lead to the stripping of volatile toxic and hazardous substances by air, resulting in secondary pollution [11]. The oxidation process (AOP), one of the technologies used in wastewater treatment, generates hydroxyl radicals (OH•), crucial oxidants in the breakdown of organic molecules. The final products of AOP include water, carbon dioxide, and various mineral ions, none of which are harmful to the environment. Despite having a high degrading capacity, AOP has drawbacks such as poor COD removal, poor stability, and expensive wastewater treatment in industrial applications. As a result, research has focused on creating novel techniques for treating water and wastewater to remove harmful industrial waste and organic chemicals [12–14].

Therefore, one alternative approach to existing wastewater treatment methods is the creation of cost-effective membranes that can adsorb PNA from aqueous solutions. Membrane processes are used as an environmentally friendly substitute to cleanse, separate, recover, or eliminate organic or inorganic components from liquid or gas media with minimal energy consumption, significantly reducing the waste volume without adding toxic compounds. The membrane technology is modular and able to work continuously. These processes apply to several economic sectors, such as the environment, energy, health, water treatment, cosmetics, food, and chemicals [15].

By using liquid membrane (LM) separation processes, a wide variety of organic and inorganic compounds can be effectively removed from aqueous solutions because of their simplicity in design, low energy costs, high selectivity, ease of operation, and ability to combine removal and recovery processes in one step. Heavy metals (although IUPAC recommends abandoning terms such as "heavy metals" [16]) are toxic environmental pollutants that accumulate in soil and water systems due to industrial discharges and agricultural runoff activities. Their presence poses significant health and environmental risks, necessitating effective recovery methods. Traditional approaches, such as chemical precipitation, coagulation, and ion exchange, often face challenges like high costs and sludge production. Advanced membrane technologies, including reverse osmosis and nanofiltration, offer improved efficiency but can be expensive and unstable.

Supported liquid membranes (SLMs) present a promising alternative due to their efficiency and cost effectiveness. SLMs require less solvent and fewer operational stages than traditional solvent extraction methods, leveraging high solute diffusion coefficients for better metal ion transport. Studies have demonstrated their effectiveness in recovering various metal ions (for example, metals belong to block d). For instance, research has shown that chelating oximes and solvating extractants like Cyanex 923 are effective for selective metal recovery. Additionally, supported ionic liquid membranes (SILMs) have been found to enhance selectivity and recovery efficiency. One study optimized SLM conditions for separating chromium (VI), copper, and zinc using D2EHPA as an extractant and acids as stripping reagents, focusing on parameters such as extraction duration and reagent concentrations. Another study developed a Fe (III) recovery model from spent alkaline batteries using Cyanex 923, highlighting SLM's economic advantages. Furthermore, SLM technology has proven effective in pre-concentrating trace metals from natural waters and detecting heavy metals like cadmium (Cd) in seawater, showcasing its versatility in environmental applications [17–20].

Among the membrane-based separation processes, León et al. used an emulsion liquid membrane process to remove PNA from aqueous solutions. This optimized the removal process by analyzing the efficiency of PNA removal from the feed phase and the initial apparent feed/membrane fluxes and permeabilities under various experiments [21]. In addition, Tao et al. simultaneously performed a two-/three-phase hollow fiber-based

liquid-phase micro-extraction (HF-LPME) method for the determination of aromatic amines in environmental water samples, including PNA.

All liquid membranes consist of an extractant agent (carrier) in an organic solvent that selectively binds to one or a class of components in the aqueous feed phase and transports it to the aqueous receiving phase through the membrane [22]. The carrier needs to be highly selective and very specific to the solution that needs to be eliminated. The most widely utilized carriers include hydro-oximes, amines, crown ethers, and phosphoorganic molecules. Carriers are mainly divided into three classes based on their functional groups: acidic, basic, and neutral:

i. Acidic Carriers: they are the most efficient at extracting the cations, as the carriers do form complex salt with cations with the exchange of protons. The acidic carriers contain COOH, P (OH), SO₃H, or chelating groups. ii. Basic Carriers: The anionic metal complexes are extracted using the alkaline/basic carriers. The best examples of such carriers are amines. iii. Neutral Carriers: For the purpose of selectively transporting various metal ions in LMs, neutral carriers are typically employed as cation carriers. They carry the metal ions in their cavities. The extraction efficiency of such neutral carriers depends on the size of their cavity and the size of the inserted ions. An anion and a cation are transported across the LM simultaneously when these carriers are employed as metal ion carriers in the membrane phase. The most common neutral carriers in LM processes are macrocyclic molecules and organic phosphoryl compounds. Tributylphosphate is a refractory molecule that is particularly difficult to degrade. Kumbasar used the separation method using emulsion liquid membranes and using TBP as an extractant. TBP is a neutral extractant. To preserve electrical neutrality, neutral extractants frequently extract cations or uncharged metal complexes together with the associated anions. Most of the neutral extractants that have been investigated in the liquid membrane studies are organophosphoryl compounds, including trioctylphosphine oxide (TOPO), TBP, and tributhylphosphine oxide (TBPO) [23–25].

TBP is the most widely used phosphatic solvent due to its high extraction selectivity [26]. It is usually used as an extractant to separate metal ions with good extraction efficiency [27]. Liu et al. used mixed carriers containing trioctylmethylammonium chloride (Aliquat 336) and TBP and used poly (vinyl) chloride (PVC) as the base polymer for the recovery of phenolic compounds from aqueous solutions [28]. The transfer of Nb (V) and Ta (V) ions in a chloride medium across a supported liquid membrane containing TBP as a carrier has been investigated [29]. Synergistic reactive extraction of platinum (IV) from aqueous solution was conducted using an organic phase consisting of TBP and bis (2, 4, 4-trimethylpentyl monothiophosphinic acid (Cyanex 302) in kerosene [30].

In this investigation, we will develop an SLM for removing an aromatic compound PNA from an aqueous solution using TBP as an extractant. An attempt has been made to optimize this technique's process parameters to obtain an efficient separation system.

2. Materials and Methods

2.1. Materials

PNA (MERCK-Schuchardt, Switzerland, \geq 99%) was dissolved in ultrapure water (Milli Q Plus Colum, Millipore, Burlington, MA, USA) to create the feed solutions (Table 1).

All chemicals used were of analytical reagent grade. NaOH (CDH, New Delhi, India, 97%), NaCl (Pacegrove, Leicestershire, UK, 99%), and sodium acetate (Loba Chemie, Mumbai, India, 99%) were used as strippants.

4-Nitroaniline	(MERCK-Schuchardt)
Chemical formula	$C_6H_6N_2O_2$
Molecular weight	$138.12 \text{ g mol}^{-1}$
Chemical structure	NH ₂ NO ₂

Table 1. Chemical formula, molecular weight, and chemical structure of 4-nitroaniline.

2.1.1. Polymeric Support

Polypropylene (Celgard 2500, Celgard Inc., Charlotte, NC, USA) was used as a polymeric support for the organic solution (Table 2).

Table 2. Physical characteristics of polymeric support.

Thickness d_0 (µm)	Pore Diameter d (µm)	Porosity ε (%)	Tortuosity ($\tau = 1 - \ln \epsilon$)
25	0.064	55	1.598

2.1.2. Extractant

The polymeric support was impregnated using TBP as a carrier. Table 3 gives the chemical formula, molecular weight, and chemical structure of TBP.

Table 3. Chemical formula, molecular weight, and chemical structure of TBP.



2.2. Membrane Preparation

Experiments on PNA extraction were performed at about 25 °C in a permeation cell. The organic liquid consisting of TBP was saturated in the membrane for 24 h, a crucial step ensuring the membrane was fully prepared for extraction. By weighing the polymeric support before and after immobilization, we determined the amount of TBP that was immobilized. An additional layer of carrier was removed by wiping it with a soft piece of paper. The obtained SLM was fixed between the two half-cells of the device, with an exposed membrane area of 3.14 cm². Source and receiving solutions (50 mL each) were placed into two compartments on the device and mixed using two magnetic stirrers. For both aqueous feeding and stripping solutions, magnetic stirring at 600 rpm at 25 °C avoided concentration polarization at membrane interfaces and in bulk solutions. The schematic illustration of the SLM process is shown in Figure 1. Using a pipette, 0.5 mL of the source and receiving solutions were removed hourly during the transport operation and diluted to a suitable volume. After that, these solutions were examined at a wavelength of 379 (Shimadzu UV–visible spectrophotometer 1650, Kyoto, Japan), and a calibration curve was used to determine the concentration of the PNA in each sample.



Figure 1. Schematic diagram of SLM process.

The E and R (%) were calculated using the following equation:

$$E\% = \frac{[PNA]_{donor,0} - [PNA]_{donor,t}}{[PNA]_{donor,0}} \times 100$$
(1)

$$R\% = \frac{[PNA]_{receiving,t}}{[PNA]_{donor,0}} \times 100$$
(2)

where $[PNA]_{donor,0}$ is the concentration of PNA in the initial source solution, $[PNA]_{donor,t}$ is the concentration of PNA in the source solution after transport, and $[PNA]_{receiving,t}$ is the concentration of PNA in the receiving phase after transport.

2.3. Buffer Solution Preparation

Table 4 describes the preparation methods of the two buffers used in this study.

Table 4. Methods for preparing buffer.

Buffer pH = 4	Buffer pH = 12	
The buffer solution (pH = 4) is prepared by	The buffer solution (pH = 12) is prepared by	
mixing a solution of succinic acid 0.2 mol L ⁻¹	mixing a solution of glycine 0.2 mol L^{-1}	
(V = 25 mL) and a solution of NaOH	(V = 25 mL) and a solution of NaOH	
0.2 mol L ⁻¹ (10 mL). Ultrapure water was	0.2 mol L^{-1} (23.35 mL). Ultrapure water was	
added to the mixture to obtain a	added to the mixture to obtain a	
100 mL solution.	100 mL solution.	

3. Results and Discussion

3.1. Transport of PNA with and without Carrier

The variation in E (%) and R (%) during the 8 h of transport is shown in Figure 2. The presence of the carrier (TBP) in the polymeric support leads to a noticeable improvement in the transport of the PNA from the feed to the receiving phase. The E (%) and the R (%) increase from 6.743 to 68.169 and from 3.053 to 49.2226, respectively, with and without impregnation. Moreover, after 8 h, the transport stops and the E (%) and R (%) remain constant. This behavior could be related to the carrier's loss from the membrane. There is a possibility that carrier losses are related to its solubility (solubility of TBP in water is 0.4 g L⁻¹ at 25 °C), as membrane liquid (ML) is not completely insoluble in an aqueous solution and some solubility exists at the ML/aqueous solutions [31,32]. In their study of TBP-mediated transport of phenol, Huidong et al. showed that emulsion formation was responsible for membrane instability [33]. Based on the thickness $d_{0,A}$, porosity ϵ_A , and tortuosity τ_A of Accurel[®] PP support, the experimental (J_{exp}) and normalized (J_N) fluxes for

PNA were calculated ($J_{exp} = 7 \times 10^{-10}$ and $J_N = 0.51 \times 10^{-10}$ mol m⁻² s⁻¹) using Celgard 2500 [24,34].

$$J_N = J_{exp} \, \frac{d_0 \tau}{\epsilon} \, \frac{\epsilon_A}{d_{0,A} \, \tau_A} \tag{3}$$

where d_0 , τ , and ϵ represent the membrane thickness, tortuosity, and porosity, respectively.

$$J_{exp} = \left(\frac{V}{A}\right) \left(\frac{dC}{dt}\right) \tag{4}$$



Figure 2. Variation in the E and R (%) as a function of the transport time. Feed solution: PNA 20 ppm; receiving solution: distilled water; membrane phase: PP-Celg without TBP and with TBP as extractant.

The receiving phase volume (L), the active area of the membrane (m²), the concentration of PNA (mol L⁻¹), and the transport time (s) are represented by *V*, *A*, *C*, and *t*, respectively. The slope $\frac{dC}{dt}$ is determined by the linear variation in the PNA concentration over time in the receiving phase.

The effect of UV radiation on transport efficiency was investigated (Table 5). Firstly, the polymeric support was irradiated with UV radiation for 15 min and 180 min, and after that, it was impregnated with TBP. The obtained system was used as a membrane phase. After 8 h of transport, the R (%) percentages were calculated and found to be 47.72% and 44.61%, respectively, for 15 and 180 min of irradiation. Therefore, the R (%) values indicate that the irradiation of the membrane with UV radiation does not affect the transport efficiency.

Table 5. Variation in the E and R (%) as a function of the transport time. Feed solution: PNA 20 ppm; receiving solution: distilled water; membrane phase: PP-Celg without TBP and with TBP as extractant.

Time of Irradiation (min)	R (%)
0	46.59
15	47.72
180	44.61

3.2. Liquid Membrane Loss

The weight of the wet and used membrane supports was measured to calculate the LM loss, and they were represented as m_{wet} and m_{used} , respectively (see Figure 3). The wet membrane indicates the polymeric support after impregnation. Following the removal, the utilized membrane was obtained. It was dried in a silica gel vessel until its mass was stable. The LM phase loss per unit area was then calculated using the following equation Δm (%) [35,36]:

LM phase loss,
$$\Delta m$$
 (%) = $\frac{m_{wet} - m_{used}}{m_{wet}} \times 100$
 Δm (%) = $\frac{0.0293 - 0.0127}{0.0293} \times 100$
 $\Delta m = 56.655$
(5)

where m_{wet} and m_{used} are the weights of the wet and used polymeric supports, respectively.



Figure 3. Real photos of PP-Celg membrane: (a) membrane before impregnation; (b) *m*_{wet}; (c) *m*_{used}.

To mitigate the leaching of TBP, we propose future studies exploring the use of other types of polymeric support, the use of alternative carriers with lower environmental impact, the addition of electrolytes in the aqueous phases, the addition of surfactants in the LM, and the application of a polymeric gel layer on the outer surface of SLM to reduce the emulsion formation. These steps aim to enhance the sustainability and industrial applicability of the SLM system.

3.3. Effect of PNA and NaOH Concentration

The percentage of PNA removal by varying initial feed phase concentration from 20 to 80 ppm is shown in Figure 4a. The removal performance was not influenced by an increase in PNA concentration. The E and R (%) are around 48.8 and 46.5%, respectively. In fact, TBP is not adequate carrier to transport PNA proportionally. It can be also attributed to carrier saturation and the smaller effective membrane area because of concentration boundary layer formation on the interface between the feed and membrane phases, which cause PNA to remain in feed phase and, accordingly, PNA pertraction remains constant at higher concentrations. Moreover, solution ionic strength at higher concentrations is more important. This also causes a lower PNA activity coefficient and hence reduces PNA activity to form complexes [37–40].



Figure 4. Variation in the E and R (%) as a function of the concentration of the PNA phase source (**a**) and (**b**) the concentration of the NaOH receiving solution at a transport time equal to 8 h.

Figure 4b illustrates the removal efficiency of PNA by varying the concentration of the stripping agent. It is clear from Figure 4b that the increase in the NaOH in the stripping phase has no impact on the transport efficiency. The E and R (%) are around 48.75% and 45.75%, respectively. Therefore, the transport of PNA from the organic-phase–receiving-phase interface occurs without any counter ion.

3.4. Selection of Stripping Agents

The receiving phase and its concentration play an important role in deciding the final recovery of the target solute by the SLM process. However, very few reports are available on the effect of stripping agents on the performance of the SLM process [41]. In this study, various stripping agents like NaOH, CH₃COONa, and NaCl were used as the receiving phase to evaluate the performance of SLM. Therefore, to achieve complete transport of PNA and avoid its back transport, we have selected a 0.01 mol L⁻¹ concentration of each stripping. The feed was kept constant at 20 ppm of PNA (pH 7), the PP polymer was impregnated with TBP, and the run time was 8 h. The E and R (%) are (47.3966, 46.59), (55.391, 50.209), (51.079, 48.201), and (50.36, 49.015) for H₂O, NaCl, NaOH, and CH₃COONa, respectively (Figure 5). The results indicated a slight E (%) increase when NaCl is used as a stripping agent. This slight increase could be explained by a better affinity to the counter ion Cl⁻ than OH⁻ and CH₃COO⁻ [42].



Figure 5. The effect of the strippants' nature on E and R (%). Feed solution: PNA 20 ppm; receiving solution: (H₂O, NaCl 0.01 mol L⁻¹, NaOH 0.01 mol L⁻¹, CH₃COONa 0.01 mol L⁻¹); organic phase: TBP; membrane (PP-Celg).

3.5. Effect of the Initial pH of the Source Phase

The effect of pH on PNA removal efficiency is shown in Figure 6. The R (%) values are 46.33, 46.59, and 46.46% for pH = 4, pH = 7, and pH = 12, respectively. The obtained values are almost equal. Hence, the initial pH of the donor phase did not influence the transport of PNA through the membrane.

At pH < 7, 4-nitroaniline would react with the H_3O^+ ions in the medium to give its conjugated acid:



The potential interaction between PNA and TBP could involve non-covalent interactions, such as hydrogen bonding or van der Waals forces, rather than traditional coordination bonds in metal complexes. PNA from the aqueous phase (aq) interacts with TBP in the organic phase (org) to form a complex in the organic phase. It is important to note
that providing a detailed and accurate representation of the complex formation is easier with specific experimental data or computational studies. The interactions between organic compounds like PNA and solvents like TBP can vary widely, and the actual behavior would need to be determined through experimental investigations or theoretical studies tailored to the specific system of interest.



Figure 6. Variation in E and R (%). Feed solution: PNA 20 ppm at different pH (pH = 4, pH = 7, and pH = 12); receiving solution: distilled water; organic phase: TBP; membrane: PP-Celg.

The mechanism of transport can be summarized in three steps [43-45]:

Step 1: Formation of a complex between PNA and TBP via hydrogen bond at the first interface feed phase-membrane;

Step 2: Migration of the formed complex through the membrane;

Step 3: Formation of a complex between water existing in the receiving phase and release of the PNA in the receiving phase.

$$[PNA]_{aq} + [TBP]_{org} \rightleftharpoons [PNA.TBP]_{org} \tag{6}$$

$$[PNA.TBP]_{org} + [H_2O] \rightleftharpoons [TBP.H_2O]_{org} + PNA$$
(7)

3.6. Membrane Stability

The reusability of the membrane was studied in two manners. Firstly, the stability of the membrane support was carried out by repeatedly using the same membrane support without further impregnation with the liquid membrane. Experimental conditions are as follows: feed phase PNA 20 ppm (pH 7), strip phase distilled water, TBP as carrier, and transport time 8 h. Fresh feed and strip solutions are used in every cycle. A total of 1 mL of each solution is taken after 8 h to find their concentrations. The R (%) calculations during four successive cycles demonstrate that the membrane is unstable. The R (%) decreases significantly from 46.59 to 5.7% for the first and last cycles. This instability could be attributed to the saturation of the membrane with PNA, slow stripping, and marginal leaching of TBP. Secondly, membrane stability was developed by re-impregnating the polymeric support with TBP after each cycle. The same experimental conditions are taken into consideration. Figure 7 reveals that the R (%) remains almost constant. Therefore, re-impregnating the membrane after each cycle improves the performance of the elaborated system. Also, this improvement confirms that the loss of the carrier is one of the reasons causing the system instability.



Figure 7. Variation in the E and R (%) per cycle. Feed solution: PNA 20 ppm; Receiving solution: distilled water; Organic phase: TBP; Membrane: PP-Celg; Cycle duration: 8 h.

3.7. Extraction Kinetics

Supported liquid membrane (SLM) transport studies were carried out by extracting PNA under ideal circumstances, 20 ppm (pH 7) of source phase concentration, distilled water in the receiving phase, carrier TBP as the organic phaser, and a duration of 8 h. PNA was extracted at room temperature and atmospheric pressure. Samples from the feed phase were taken every hour and analyzed using UV spectrophotometry. The evaluation of the PNA extraction kinetics under the operational conditions was estimated by fitting the time-course performance data with the first-order linearized reaction by the following equation [46,47]:

$$\operatorname{Ln}\frac{C_t}{C_0} = -K_a t \tag{8}$$

where [PNA]_{donor,t} the feed phase concentration at time *t*, [PNA]_{donor,0} is the initial feed phase, and K_a is the apparent rate constant. A plot of ln C_t/C_0 versus time shows a straight line having a slope of 5.28×10^{-5} (Figure 8). Hence, the extraction of PNA using SLM follows first-order kinetics with the apparent rate constant $K_a = 5.28 \times 10^{-5} \text{ s}^{-1}$.



Figure 8. First-order plot for extraction of PNA.

4. Conclusions

In conclusion, this study elucidates the potential of supported liquid membrane (SLM) technology for the removal of 4-Nitroaniline (PNA) from aqueous solutions, addressing the pressing environmental concerns posed by this toxic compound. Through systematic experimentation and optimization, we identified key factors influencing the transportation efficiency of PNA, including source phase concentration, pH, choice of carrier, and stripping agents. Our results demonstrate that under optimal conditions, the extraction and re-extraction percentages are around 50%. The developed system exhibits first-order linearized reaction kinetics.

Furthermore, the stability of the membrane and the extent of liquid membrane loss were evaluated, shedding light on practical considerations for the implementation of SLM systems in real-world applications. While membrane stability proved to be a challenge, particularly in terms of carrier leaching and saturation, strategies such as re-impregnation of the membrane with tributyl phosphate (TBP) after each cycle showed promise in improving system performance.

Author Contributions: Methodology, N.K.; validation, N.K.; formal analysis, H.T. and A.A. (Abrar Alnafisah); investigation, A.A. (Azizah Algreiby) and L.B.; writing—original draft, L.A.; writing—review and editing, A.A. (Azizah Algreiby) and N.K.; supervision, A.A. (Azizah Algreiby) and N.K. All authors have read and agreed to the published version of the manuscript.

Funding: The Researchers would like to thank the Deanship of Graduate Studies and Scientific Research at Qassim University for financial support (QU-APC-2024-9/1).

Data Availability Statement: The original contributions presented in the study are included in the article; further inquiries can be directed to the corresponding author.

Conflicts of Interest: The authors declare no conflicts of interest.

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Ekaterina Bondar *, Elena Dmitriyeva *, Igor Lebedev, Anastasiya Fedosimova, Aigul Shongalova, Sayora Ibraimova, Ainagul Kemelbekova, Ulzhalgas Issayeva, Bagdat Rakymetov and Bedelbek Nurbaev

> Institute of Physics and Technology, Satbayev University, Ibragimov 11, Almaty 050013, Kazakhstan; lebedev692007@yandex.ru (I.L.); ananastasia@list.ru (A.F.); shongalova.aigul@gmail.com (A.S.); sayara_ibraimova@mail.ru (S.I.); a.kemelbekova@sci.kz (A.K.); ulyajan_1603@mail.ru (U.I.); bagdat_r@mail.ru (B.R.); bedel.armia.99@gmail.com (B.N.)

* Correspondence: bondar@sci.kz (E.B.); dmitriyeva2017@mail.ru (E.D.)

Abstract: This article presents the results of the formation of hierarchical micro–nano structures in nanostructured tin dioxide films obtained from the lyophilic film-forming system $SnCl_4/EtOH/NH_4OH$. The classification of the shape and size of the synthesized structures, in relation to the pH of the solution, is presented. Measurements were carried out on an X-ray diffractometer to study the crystal structure of the samples analyzed. It was found that SnO_2 and NH_4Cl crystallites participate in the formation of the synthesized hierarchical structures. It is shown that the mechanism of the formation of hierarchical structures depends on the amount of ammonium hydroxide added. This makes it possible to control the shape and size of the synthesized structures by changing the ratio of precursors.

Keywords: nanostructures; thin films; sol-gel chemistry; X-ray diffraction; crystal structure

1. Introduction

Metal oxides (SnO₂, ZnO, TiO₂, In₂O₃, etc.) represent a rather interesting class of materials for fundamental research, since they have a wide range of electrical and optical properties [1].

Composite systems based on tin dioxide, as a functional material, have many applications [2–4]. The high chemical homogeneity of the obtained products allows the use of SnO_2 coatings as three-dimensional macroporous anodes in lithium-ion batteries [5], as active layers in gas analysis equipment, as protective coatings against corrosion, etc. [6–8].

It should be noted that thin films of undoped SnO_2 quickly see their properties deteriorate when heated above 500 °C since they are in a metastable phase. Doping SnO_2 with various chemical elements (F, Sb, Ga, Pd, Fe, Si, Ni, Gr, Au, etc.) can significantly change its electrical, optical, and gas-sensitive properties, as well as any other properties [9–13]. It also expands the application possibilities of thin films made of tin dioxide. In addition, the properties of these films can be improved by treating them with various types of plasma [14,15].

One of the distinctive characteristics of nanosized tin dioxide films is their combination of high electrical conductivity with transparency in the visible and ultraviolet radiation regions. Oxygen non-stoichiometry has a direct effect on the functionality of oxides. In turn, the technology of oxide production and its subsequent processing have large roles in oxygen non-stoichiometry [16,17]. The pH of film-forming systems plays an important role in determining the structure and properties of the resulting films. Systems with a pH range of 7–11 are often considered in studies [18]. In this work, the pH range of 1.4–1.53 was studied. In this range, changes in light absorption and surface resistance are observed, so that there is a transition from the formation of surface SnO_2 to the formation of bulk SnO_2 [19]. The advantage of a comprehensive study is the dependence of the transparency

Citation: Bondar, E.; Dmitriyeva, E.; Lebedev, I.; Fedosimova, A.; Shongalova, A.; Ibraimova, S.; Kemelbekova, A.; Issayeva, U.; Rakymetov, B.; Nurbaev, B. The Synthesis of Materials with a Hierarchical Structure Based on Tin Dioxide. *Nanomaterials* **2024**, *14*, 1813. https://doi.org/10.3390/ nano14221813

Academic Editors: Jose Maria De Teresa, Ricardo Lopez Anton and Sion Federico Olive Méndez

Received: 20 September 2024 Revised: 5 November 2024 Accepted: 7 November 2024 Published: 13 November 2024



Copyright: © 2024 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). of the samples and their resistance on the change in the pH of the film-forming system, which is very important for solar cells and gas sensors.

In recent years, a type of material that can be called functional hierarchical material has clearly emerged in the field of functional materials. Such materials consist of elements of several scales, which are organized in such a way that elements of a smaller scale are inserted into elements of a larger scale. The main mechanism for the formation of hierarchical nanomaterials is self-assembly. Materials with a hierarchical structure have significant potential for practical applications [20–25].

Hierarchical structures based on SnO₂ are intensively studied, since they have a large surface area, high surface permeability, low density, low cost, environmental friendliness, and stable physical and chemical characteristics [26].

This work presents the possibility of synthesizing thermally stable hierarchical micro– nano structures with adjustable sizes, which depend on the ratio of ammonium ions to tin ions in the film-forming system SnCl₄/EtOH/NH₄OH, using sol–gel technology.

2. Materials and Methods

The following reagents were used to conduct an experiment on the synthesis of filmforming systems:

- Tin chloride pentahydrate powder SnCl₄·5H₂O;
- Ethyl alcohol C₂H₅OH (GOST 5962-13);
- (3) Concentrated aqueous solution of ammonia NH₄OH.

A total of 4 film-forming solutions were prepared using the sol–gel method. For the preparation of these solutions, the following components were used:

- (1) $m(SnCl_{4.5}H_2O) = 3.9072 \text{ g}.$
- (2) $V(C_2H_5OH) = 100 \text{ mL}.$
- (3) $V(NH_4OH) = 0 mL; 0.4 mL; 0.8 mL; 1.6 mL.$

 $SnCl_4$ · $5H_2O$ powder was poured into a flask V = 100 mL and dissolved in ethyl alcohol V = 50 mL. Next, ethyl alcohol V = 25 mL was poured into a separate flask and the required amount of concentrated aqueous ammonia solution was added. The resulting solution was introduced into the original flask drop by drop. Then, the remaining volume of ethyl alcohol was poured in and mixed thoroughly, and the solution was sent to a dark place for a day to "mature".

Table 1 shows the amount of added ammonia, the pH of the solution after maturation, and the ratio of ammonium ions to tin ions.

V(NH ₄ OH), mL	pH of Film-Forming Systems	Tin Ions in 100 mL (in Moles)	Ammonium Ions in 100 mL (in Moles)	Ammonium/Tin Ratio
0	1.40	0.011	0	0
0.4	1.44	0.011	0.005	0.455
0.8	1.46	0.011	0.01	0.909
1.6	1.49	0.011	0.02	1.818

Table 1. Ratio of ammonium ions to tin ions in film-forming systems.

The following chemical reactions occur in the systems:

$$SnCl_4 + 4C_2H_5OH \rightarrow Sn(OH)_4 + 4C_2H_5Cl \tag{1}$$

$$SnCl_4 + 4H_2O \rightarrow Sn(OH)_4 + 4HCl$$
 (2)

$$\frac{T, \ ^{\circ}C}{Sn(OH)_4} \rightarrow SnO_2 + 2H_2O$$
(3)

When interacting with a concentrated aqueous solution of ammonia, the following reactions occur:

$$\operatorname{SnCl}_4 + \operatorname{NH}_4\operatorname{OH} \to \operatorname{Sn}(\operatorname{OH})_4 + 4\operatorname{NH}_4\operatorname{Cl}$$
 (4)

$$NH_4OH + HCl \rightarrow NH_4Cl + H_2O$$
 (5)

The synthesized samples were annealed at 400 °C for 15 min.

3. Results and Discussion

The synthesized samples were examined using an optical microscope, a Raman spectroscope Solver Spectrum (NT-MDT, Moscow, Russia), an X-ray diffractometer DRON-6 Burevestnik (St. Petersburg, Russia), and a scanning electron microscope (SEM) JEOL (JSM-6490LA, Tokyo, Japan).

3.1. Optical Microscopy

To find non-transparent objects in the synthesized samples, studies were carried out using an MPE-11 optical microscope. Figure 1 shows photographs of the films obtained from the film-forming system SnCl₄/EtOH/NH₄OH using different ratios of ammonium ions to tin ions.



Figure 1. The structure of the film obtained from the film-forming system SnCl₄/EtOH/NH₄OH via the sol–gel method: (**a**) without adding NH₄OH; (**b**) 0.4 mL NH₄OH per 100 mL of solution; (**c**) 0.8 mL NH₄OH per 100 mL of solution; (**d**) 1.6 mL NH₄OH per 100 mL of solution.

It can be seen in Figure 1 that, in the absence of ammonium hydroxide (Figure 1a), no regular structures are detected in the film. When ammonium ions are added, certain structures begin to form, the shape and size of which depend on the relative amount of tin ions N(Sn) and ammonium ions N(NH₄).

At N(Sn) > N(NH₄), structures resembling a six-petal flower are formed (Figure 1b). The average size of the synthesized structures reaches 40 μ m.

At N(Sn) < N(NH₄), the formation of cross-shaped structures predominates (Figure 1d). Their size is significantly higher than that of the flower-like structures and reaches more than 300 μ m.

When the number of tin ions is approximately the same as the number of ammonium ions, some mixed structures are obtained that resemble neither a cross-shaped structure nor a six-petal flower (Figure 1c).

3.2. Raman Spectroscopy

Raman spectra of the samples were obtained at room temperature, with a laser wavelength of 473 nm and a spectral resolution of 4 cm⁻¹, using Solver Spectrum (NT-MDT, Moscow, Russia).

Figure 2 shows the Raman spectra of the synthesized samples with and without the addition of NH₄OH. The spectra of the samples show an intense broad band at 565 cm⁻¹ and a less intense band at 770 cm⁻¹. These bands can be ascribed to the vibrational modes of amorphous SnO₂ according to [27].



Figure 2. Raman spectra of the sample: (a) without adding NH₄OH; (b) 1.6 mL NH₄OH per 100 mL of solution.

The spectra are very similar and therefore do not allow us to identify any distinctive features in the formation of the synthesized films.

3.3. X-Ray Diffraction

To study the crystal structure of the films obtained, measurements were carried out on a DRON-6 X-ray diffractometer (Burevestnik, St. Petersburg, Russia). The data obtained were processed using the ASAS method [28]. The results are presented in Figure 3.

In Figure 3a, which shows the X-ray diffraction pattern of the sample without NH_4OH addition, three clear peaks emerge from the crystallographic planes of tin dioxide $SnO_2(110)$, $SnO_2(101)$, and $SnO_2(211)$.

In Figure 3b, a peak emerging from the crystallographic plane of ammonium chloride $NH_4Cl(110)$ is visible. The signals from three crystallographic planes, namely, $SnO_2(110)$, $SnO_2(101)$, and $SnO_2(211)$, are also highlighted. Unfortunately, the SnO_2 peaks in the X-ray diffraction spectra shown in Figure 3b are not as clear as those shown in Figure 3a. This is explained by the texturing effect: the peaks from tin dioxide, which have a relatively low intensity, are superimposed on the peak from ammonium chloride, which is several times more intense.



Figure 3. X-ray diffraction pattern of the crystal structure of the film obtained from the film-forming system SnCl₄/EtOH/NH₄OH by the sol–gel method, measured on a DRON-6 X-ray diffractometer: (a) sample without NH₄OH; (b) sample with NH₄OH.

The average crystallite sizes were calculated using the Scherrer formula, which relates the crystallite sizes to the width of the diffraction peaks [29]. The SnO_2 crystallite size is 3.6 nm, and the NH₄Cl crystallite size is 109 nm.

Thus, SnO_2 and NH_4Cl crystallites participate in the formation of the synthesized hierarchical structures. In order to try to explain the correlation between the characterized samples and optical microscope images in relation to the amount of ammonium ions, we propose the consideration of the elementary cells of SnO_2 and NH_4Cl , which are presented in Figure 4.





The unit cell of SnO_2 , in which six tin atoms are bonded to nine oxygen atoms, visually resembles a six-petal flower. And the unit cell of NH₄Cl resembles a cross of four hydrogen atoms attached to a nitrogen atom. It can be assumed that, at low NH₄OH concentrations, the dominant basis for the formation of the synthesized hierarchical structures is the unit cells made of SnO₂. At high NH₄OH concentrations, a significant contribution is made by the unit cells of NH₄Cl.

As an explanation for the association of the "flower" and "cross" morphologies on a scale of several micrometers in a single-crystal structure, the presence of a fractal construction of the structures shown in Figure 1b–d is assumed. As an example, Figure 5a shows a Julien fractal aggregate, in which a six-petal structural element forms a six-petal object of a larger size [30]. There is a certain initial particle in the center of the aggregate, and the other six particles are attached to it. In this case, all particles are identical, moving along the positive and negative directions of the three basis vectors of the lattice. The first stage of such an aggregate is an initial ensemble of seven particles. At the second stage, the same "flowers" are attached to six sides, and so on. That is, the main property of



fractal aggregates is self-similarity [31–33]. Figure 5b shows a two-dimensional disordered aggregate, in which the cross morphology is formed from a cruciform structural element.

Figure 5. (a) Julien fractal aggregate; (b) two-dimensional disordered aggregate.

The addition of NH₄OH significantly affects the structure of the films. Tin tetrachloride $SnCl_4$ dissolves in ethyl alcohol C_2H_5OH . As a result, a highly dispersed colloidal system (sol) is formed. In colloidal systems, dispersed particles do not precipitate. In a suspended state, they are maintained by Brownian motion [34–36]. But unlike what occurs under the usual Brownian motion of particles, dispersed particles in colloidal solutions cannot meet under normal conditions, which is due to them having the same charge as the particles of the dispersed phase. The addition of ammonium hydroxide leads to the deformation of the electric layer of the dispersed phase. This accelerates the coagulation process. During sol coagulation, tin hydroxide Sn(OH)₄ is formed, which has a gel-like structure. Unstable Sn(OH)₄ decomposes with the formation of water and tin dioxide. In addition, as shown in Figure 3b, NH₄Cl, which is formed during chemical reactions (4) and (5), is incorporated into the film's structure. This leads to a change in the shape of the synthesized structures.

Thus, the mechanism of the formation of hierarchical structures depends on the amount of ammonium hydroxide added. This makes it possible to control the shape and size of the synthesized structures by changing the ratio of precursors.

3.4. Scanning Electron Microscopy (SEM)

To better understand the distribution of tin in the obtained samples, we mapped them using SEM. The results are shown in Figure 6.

The gradation of the mapping scale is shown on the left in Figure 6, moving from black to red, pink, and crimson colors. This shows the level of tin content in the sample areas. As can be seen from Figure 6a, the film synthesized from the film-forming solution without additives shows a uniform distribution of tin throughout the sample, since the entire area of the analyzed sample is covered uniformly with multi-colored dots associated with the tin content scale. When forming structures resembling a six-petal flower (Figure 6b), the greatest accumulation of tin is observed precisely in the area of these structures. The middle of these structures is highlighted in crimson and red, with yellow and green colors seen along the edges. This indicates that, in these places, the concentration of tin is the highest. Conversely, the rest of the sample area is marked in black, blue, and light blue colors. This indicates the lower tin content in this area. With a further increase in the ammonia content in the solution (Figure 6c,d), a decrease in the tin content is observed near the cruciform structures. This confirms our assumption, outlined in Section 3.3, about the formation of hierarchical structures from SnO₂ and NH₄Cl crystallites. That is to say, the size and shape of the hierarchical structures depend on the relative amounts of tin ions and ammonium ions.



Figure 6. The mapping of samples obtained from the film-forming system SnCl₄/EtOH/NH₄OH with different additive contents: (**a**) without additive; (**b**) 0.4 mL NH₄OH per 100 mL of solution; (**c**) 0.8 mL NH₄OH per 100 mL of solution; (**d**) 1.6 mL NH₄OH per 100 mL of solution.

4. Conclusions

Thermally stable hierarchical micro–nano structures were synthesized from the filmforming system $SnCl_4/EtOH/NH_4OH$ using sol–gel technology. The use of the filmforming system $SnCl_4/EtOH/NH_4OH$ allows us to create hierarchical micro–nano structures with an adjustable (depending on the pH of the solution) size. The discovered relationship between the technological factors and the film's structure has significant practical value for the formation of gas-sensitive layers of the material. To develop a better understanding of the tin distribution in the samples obtained, they were mapped. When forming structures resembling a six-petal flower, the greatest accumulation of tin is observed precisely in the area of these structures. With a further increase in the ammonia content in the solution, a decrease in the tin content is observed near the cruciform structures, which confirms our assumption about the formation of the synthesized hierarchical structures in such films being due to the presence of NH_4Cl ions. The synthesized hierarchical structures may increase the gas sensitivity of the sensors of various gasses. These studies require further careful experiments.

Author Contributions: Conceptualization, I.L. and E.D.; methodology, I.L., E.D. and A.F.; formal analysis, E.B., A.F. and A.S.; investigation, E.B., S.I., A.K., U.I. and B.N.; resources, B.R.; data curation, I.L. and E.D.; writing—original draft preparation, E.B., I.L. and A.S.; writing—review and editing, E.B. and I.L.; visualization, A.F., A.S. and U.I.; supervision, I.L.; project administration, E.B.; funding acquisition, E.B. and I.L. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Science Committee of the Ministry of Education and Science of the Republic of Kazakhstan, grant number AP19574404.

Data Availability Statement: The original contributions presented in the study are included in the article, further inquiries can be directed to the corresponding author.

Conflicts of Interest: The authors declare no conflicts of interest.

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ISBN 978-3-7258-3034-3